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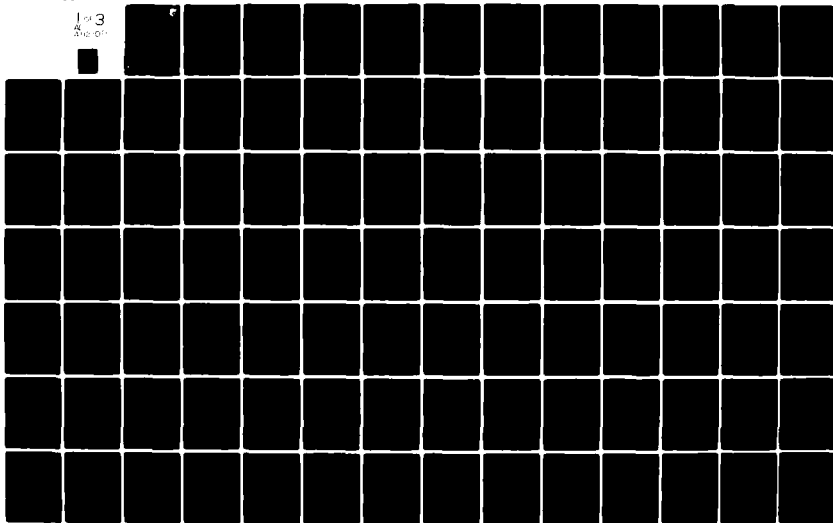
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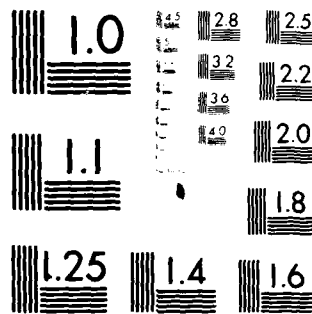
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RESEARCH AND DEVELOPMENT ON WEAR METAL ANALYSIS

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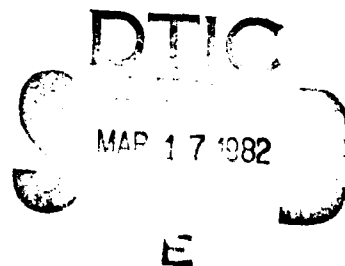
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FINAL REPORT FOR PERIOD MARCH 1976 - JULY 1981

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MATERIALS LABORATORY
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This technical report has been reviewed and is approved for publication.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The reliability of wear metal determinations depends on the integrity of the primary standards employed to calibrate the instruments, Therefore, standards were synthesized and evaluated for use in the Oil Analysis Program. The standards currently used by the Air Force, in addition to Cannon, metal caprates, metal β -diketonates, and NBS standards were evaluated for their long term stability.		

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Two state-of-the-art plasma emission instruments were evaluated for their potential applications to the ~~Air Force Oil Analysis Program~~. The goal of this effort was to improve the particle detection capability of oil analysis instruments. The sample introduction systems, ~~employed~~ by these instruments could not efficiently transport particles to the plasma sources. However, the dc plasma instrument could analyze particles better than currently used instruments.

Research was also conducted in order to identify and characterize wear debris found in typical used turbine engine lubricating oils. Methods were developed to determine the concentration of organometallic, metallic and metal oxide species in oils for Mg, Cu and Fe.

An investigation was conducted in order to determine and recommend optimized atomic absorption procedures for the analysis of wear metals in aircraft lubricating oils. The optimization procedures and recommended AA methods are included, in the report.

A method was developed to determine the "actual" concentration of wear metals in authentic used aircraft engine oils. The method involves adding an acid mixture to the oil sample to dissolve any metallic particles present. The oil/acid mixture is diluted and a surfactant added to provide a homogeneous sample suitable for analysis by atomic absorption spectrometry. The method is quantitative for Al, Cr, Cu, Fe, Mg, Mo, Ni, Pb, Sn and Ti metallic particles.

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FOREWORD

This report describes the research and development on wear metal analysis conducted by personnel of the University of Dayton Research Institute on Contract No. F33615-76-C-5312 and task no. 2303Q203. The work was conducted at the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio with Dr. Kent J. Eisentraut as the project monitor.

The work reported herein was performed during the period from March 16, 1976 to July 20, 1981 and is the Final Report for the above mentioned contract.

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GLOSSARY OF TERMS

1. Analyte. The element being analyzed.
2. Atomic Absorption Spectrometry. An analytical method for the determination of elements, based on the absorption of radiation by free atoms.
3. Atomic Emission Spectrometry. An analytical method for the determination of elements based on the emission of radiation by excited atoms.
4. Atomic Vapor. A vapor that contains free atoms of the elements being analyzed.
5. Atomization. The process that converts the analyte element, or its compounds, to atomic vapor.
6. Atomizer. The device used to produce a population of free atoms.
7. Blank Solution. A solution that does not contain the analyte, but in other respects has, as far as possible, the same composition as the sample and standard solutions.
8. Burner Angle. The acute angle between the plane of the flame produced by a long path burner and the optical axis of the monochrometer.
9. Carrier Gas. The gas used to carry the sample mist to the atomizer.
10. Characteristic Radiation. Radiation that is specifically emitted or absorbed by free atoms of the element being analyzed.
11. Concomitant Elements. Elements that accompany the analyte.
12. Depression. An interference that causes a decrease in the measured signal.

13. Direct Current Plasma Jet. A plasma discharge generated between electrodes by a low voltage (40V) direct current in a flowing, conducting gas (argon).
14. Enhancement. An interference that causes an increase in the measured signal.
15. Flame Atomization Efficiency. The ratio of the amount of analyte converted to free atoms in the atomizer to the total amount of analyte entering the nebulizer.
16. Flow Spoiler. A device, in a spray chamber, for removing large droplets from the mist.
17. Fuel. The substance, usually a gas, which is burnt to provide the atomizing flame.
18. Grating. A polished surface ruled with equidistant and parallel lines and is used to disperse light by diffraction.
19. Hollow Cathode Lamp. A discharge lamp with a hollow cathode, usually cylindrical, used in atomic spectroscopy to generate characteristic radiation.
20. Inductively Coupled Plasma. A plasma discharge generated by a high frequency current (27.2 MHz) in a flowing, conducting gas (argon).
21. Interference. A general term for an effect which alters the population of free atoms and, therefore, the measured signal produced by a particular concentration of the element being analyzed.
22. Matrix Effect. An interference caused by differences between solutions of a sample and a standard containing only the element being analyzed.
23. Monochromator. The device used to isolate the desired single wavelength of radiation emitted by the hollow cathode lamp.

24. Nebulization. The process that converts a liquid to a mist.
25. Nebulization Efficiency. The ratio of the amount of sample reaching the atomizer to the total amount of sample entering the nebulizer.
26. Nebulizer. A device for the production of an aerosol from a liquid.
27. Observation Height. The vertical distance between the optical axis of the monochromator and the top of the burner.
28. Optical Axis of the Monochrometer. The light beam emitted from the hollow cathode lamp represents the optical axis of the monochrometer when the light beam is aligned so that maximum intensity is observed on the energy meter.
29. Oxidant. The substance, usually a gas, used to oxidize the fuel in the flame.
30. Plasma. A high-temperature, ionized, conducting gas.
31. Sample Introduction System. The part of an atomic absorption spectrometer usually consisting of a nebulizer, a spray chamber, and a burner head which accepts the sample and prepares it for atomization.
32. Sample Solution. The sample dissolved in a solvent.
33. Standard Solution. A solution which has the same solvent as the sample and which contains the analyte in known concentrations.
34. Spray Chamber. The vessel where the sample mist, oxidant and fuel are mixed prior to transfer to an atomizer.
35. Used Oil Samples. Samples obtained from operational aircraft which were classified as follows;

HIGH PPM. Oil samples contained abnormally high concentrations of wear metal but abnormal engine component wear was not verified.

HIT. Oil sample contained abnormally high concentrations of wear metal and abnormal wear was verified by inspection.

FAILURE. Oil sample obtained from an engine which failed undetected by OAP.

ROUTINE. Oil sample contains normal concentration of wear metal.

36. Working Curves. The relationship between the measured signal and the standard solution concentrations. The analyte working curve is generally established by making measurements on a series of standard solutions and plotting the absorbance or emission vs. the standard concentrations.

LIST OF ABBREVIATIONS

AA	Atomic Absorption
AAS	Atomic Absorption Spectrometry
AES	Atomic Emission Spectrometry
AEE	Atlantic Equipment Engineers
A/E35U-1	Rotating Disk Electrode Atomic Emission Spectrometer, used prior to the A/E35U-3
A/E35U-3	Rotating Disk Electrode Arc/Spark Atomic Emission Spectrometer currently used for oil analysis
DCP	Direct Current Plasma
FAS-2PL	Inductively coupled plasma emission spectrometer
HGA-2100	Graphite furnace atomizer
ICP	Inductively Coupled Plasma
JOAP	Joint Oil Analysis Program
NAS	Naval Air Station
OAP	Oil Analysis Program
PE305B	Perkin-Elmer's atomic absorption spectrometer, Model No. 305B
RDE	Rotating Disk Electrode
ROC/RIC	Research Organic/Inorganic Chemical Corporation
SMI-III	Direct current plasma emission spectrometer
TSC	Technical Support Center
VMC	Vacuum Metallurgical Company
Ag	Silver
Al	Aluminum
B	Boron
Ba	Barium

LIST OF ABBREVIATIONS
(Concluded)

Be	Beryllium
Cd	Cadmium
Cr	Chromium
Cu	Copper
Fe	Iron
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
Na	Sodium
Ni	Nickel
Pb	Lead
Si	Silicon
Sn	Tin
Ti	Titanium
V	Vanadium
Zn	Zinc
HCl	Hydrochloric Acid
HF	Hydrofluoric Acid
HNO ₃	Nitric Acid
MeOH	Methanol
N ₂ O	Nitrous Oxide
MIBK	Methyl Isobutyl Ketone
<	Less Than
>	Greater Than

SECTION I

INTRODUCTION

This report prepared by the University of Dayton Research Institute is the Final Report on research and development for the Air Force Oil Analysis Program. Oil analysis is a technique which monitors wear within the equipment's oil-wetted system by determining the concentration of wear metal in samples of the equipment's lubricant. The wear metals are generated by the moving surfaces of the metallic components within the lubricated system. Wear metal analysis coupled with the knowledge of the metallurgy of the oil wetted components allows one to identify the wearing component and replace it before failure occurs.

The reliability of wear metal determinations depends on the integrity of the primary standards employed to calibrate the instruments. Therefore, the standards used by the Air Force were evaluated for their long term stability. In addition to the Air Force standards, Conostan, Cannon, metal caprates, metal β -diketonates and NBS standards were evaluated for their suitability to Air Force operations. Synthesis of other possible standards was also investigated. Emphasis was placed on the development of molybdenum and titanium oil soluble standards since standards for these two elements are not readily available. The work on standard synthesis is reported in Section II while the evaluation of standards for their long term stability is discussed in Section III.

State-of-the-art emission instruments and new analytical techniques were studied for potential applications to the Air Force Oil Analysis Program. The goal of this effort was to improve the particle detection capabilities of the oil analysis methods. The results of this work are summarized in Section IV.

Work was also carried out to identify and characterize the wear debris found in used lubricating oils. The work conducted in this area is reported in Section V.

Atomic absorption instruments are used for the determination of wear metals in about 20 OAP laboratories. To provide the Air Force with AA procedures for wear metal analyses, the AA procedures were investigated and optimized. The recommended AA procedures are given in Sections VI and VII.

SECTION II

DEVELOPMENT OF ANALYTICAL STANDARDS

The problem of finding additional sources (other than Conostan) of suitable oil soluble compounds for use as standards has increased since the determination of additional trace contaminants, such as Ti and Mo, has been required. Many organometallic compounds are not satisfactory standards because they are not sufficiently soluble in petroleum products or are not compatible with the oil. Ideally, the organometallic compounds should be stable stoichiometric substances and soluble in a wide variety of organic liquids to give stable standard solutions. Also, these compounds should be readily obtainable or easily prepared and purified in the laboratory and should be compatible with other organometallic compounds since multielement standards are normally required.

1. DEVELOPMENT OF AN ORGANOMETALLIC MOLYBDENUM STANDARD

Pursuant to our objectives to develop a molybdenum standard, we prepared several molybdenum compounds. The reactions studied appear in Table 1.

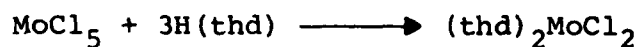
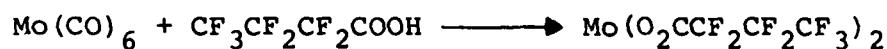
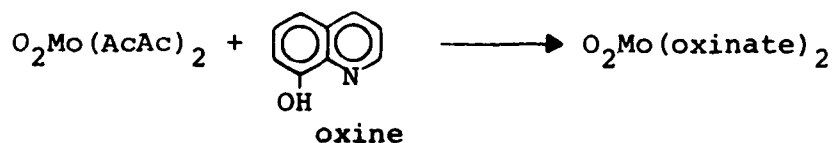
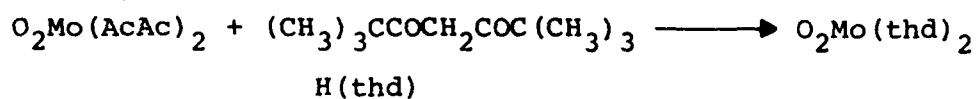
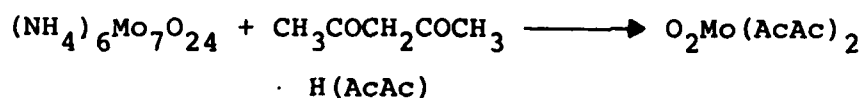
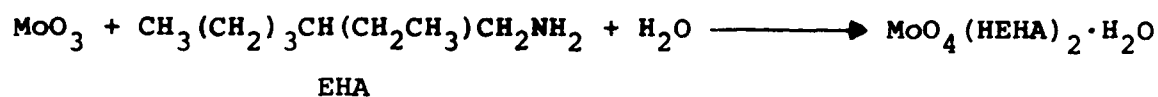
a. Experimental

(1) Bis (2-ethylhexylammonium)molybdate(VI)

A 2-gram sample of molybdic anhydride (99.5% MoO_3) was placed in a 50-ml beaker, and 10 ml of 2-ethylhexylamine and 5 ml of water were added. The mixture was heated until the MoO_3 dissolved. The excess water and 2-ethylhexylamine were evaporated, leaving a white solid. The infrared spectrum of the white solid (Figure 1) shows bands at 2500, 2150, 1615, and 1520 cm^{-1} which is characteristic of an amine salt.⁽¹⁾ The absorption band at 3500-3400 cm^{-1} indicates the presence of water in the product. Elemental analysis gave:

Obs.	43.94%C	9.61%H	18.3% Mo
Calc.	43.8%C	9.59%H	21.9% Mo

TABLE 1
SYNTHESIS OF ORGANOMETALLIC MOLYBDENUM COMPOUNDS



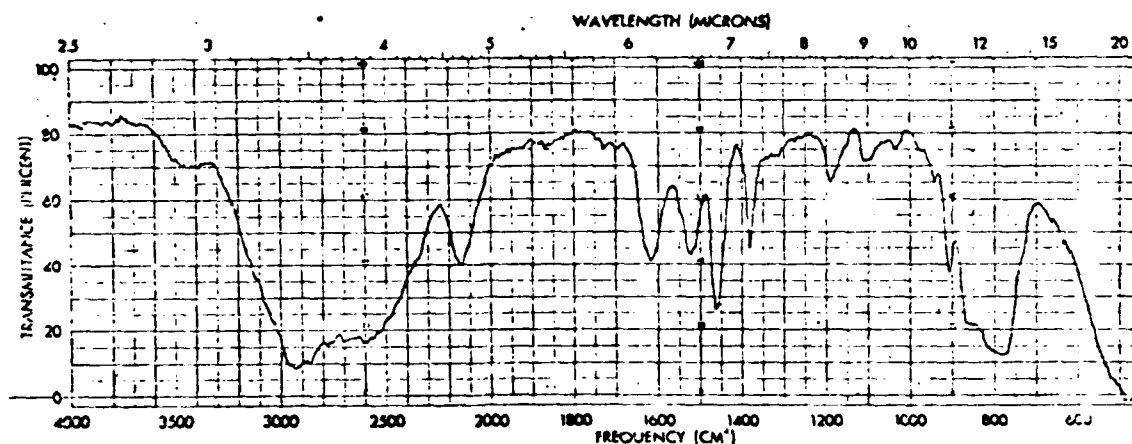


Figure 1. Infrared Spectrum of $[\text{C}_8\text{H}_{17}\text{NH}_3]_2 \text{MoO}_4 \cdot \text{H}_2\text{O}$ (Nujol).

(2) Bis(2,4-pentanedionato)dioxomolybdenum(VI)

A 0.02-mole sample of ammonium paramolybdate was dissolved in 50 ml of water, and 10 ml of acetylacetone was added. The resulting solution was acidified dropwise with 1 M H_2SO_4 until a yellow solid precipitated. The yellow solid was isolated by filtration and air dried. The product was purified by recrystallizing from acetylacetone giving a yellow crystalline product decomposing at $177\text{--}179^\circ\text{C}$ (Lit $179^\circ\text{C}^{(2)}$, $186^\circ\text{C}^{(3)}$). The infrared spectrum is shown in Figure 2a.

(3) Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)dioxomolybdenum(VI)

A 0.5-gram sample of $\text{O}_2\text{Mo}(\text{AcAc})_2$ was dissolved in $\text{H}(\text{thd})$ and heated to 100°C for several hours. The resulting liquid was diluted with heptane and crystals began to form. The crystals were isolated by filtration and recrystallized from heptane which contained a few drops of $\text{H}(\text{thd})$ to stabilize the product. The infrared shows bands due to thd and MoO_2 groups and is shown in Figure 2b (MP $131\text{--}133^\circ\text{C}$).

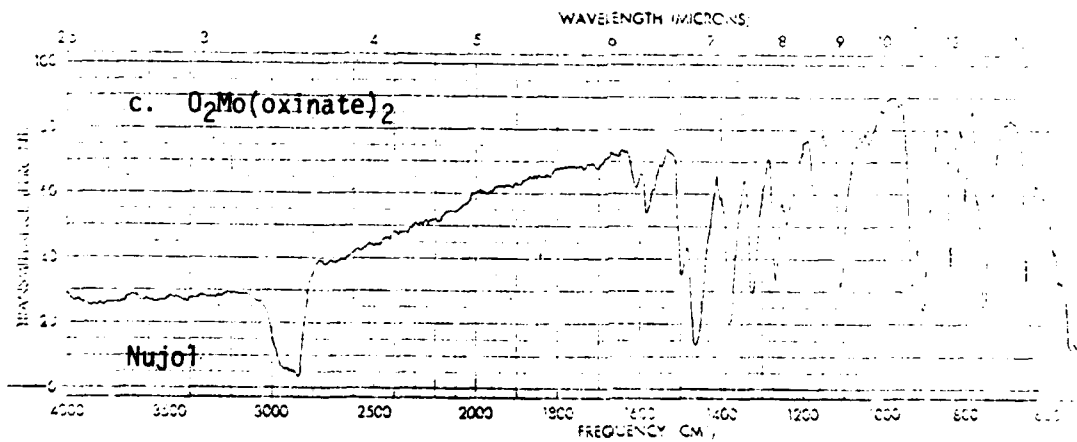
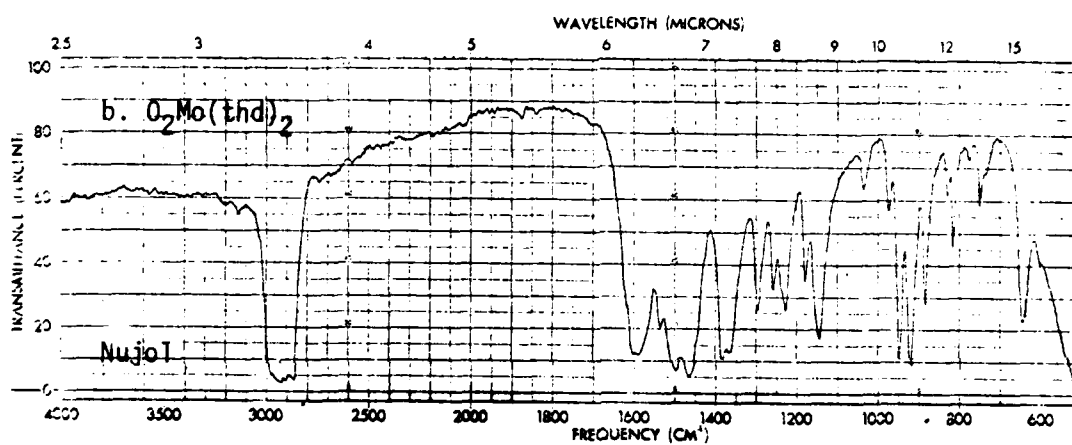
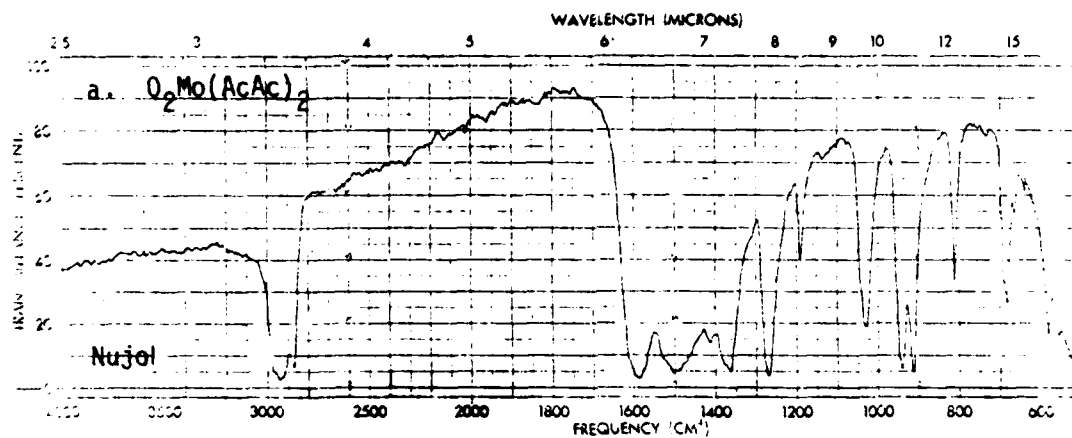


Figure 2. Infrared Spectra of Molybdenyl Compounds

(4) Bis(8-oxinate)dioxomolybdenum(VI)

A 0.001-mole sample of $O_2Mo(AcAc)_2$ was dissolved in acetylacetone, and 0.002 mole of 8-hydroxyquinoline was added. A yellow crystalline product began to form immediately. The yellow product was isolated by filtration. The infrared spectrum shown in Figure 2c is indicative of 8-hydroxyquinoline and MoO_2 groups (MP $345-354^\circ C$; Lit. $356-361^\circ C$ ⁽⁴⁾).

(5) Mo Standard from MoO_3

A 0.3838g sample of MoO_3 was solubilized in a mixture of 9g of 2-ethylhexylamine and 1.25g water. This solution was then diluted with Mobil ester oil to give 62.55g of a solution containing 4000 ppm Mo. Different amounts of this solution were diluted with Mobil ester oil to obtain standard solutions containing 100, 45, 30 and 10 ppm.

(6) Mo Standard from $Mo(CO)_6$

Molybdenum hexacarbonyl was solubilized in a minimum quantity of heptafluorodimethyloctanedione [H(fod)] and 2-ethylhexanoic acid with gentle heating and diluted with Mobil ester oil to obtain a solution containing 100 ppm Mo. Different amounts of this solution were used to prepare 50 and 10 ppm Mo standards in Mobil 7808 oil.

(7) Molybdenum(II) heptafluorobutyrate

One gram of $Mo(CO)_6$ was mixed with 15g of heptafluorobutyric acid in a 50-ml round-bottom flask equipped with a reflux condenser. The reaction mixture was refluxed until gas evolution ceased (~ 20 hrs). The reaction mixture turned from clear to yellow and finally black. The reaction products were allowed to cool to room temperature and then extracted with three 20-ml portions of hot toluene. The volume of toluene was reduced by heating and then allowed to cool. The yellow needles which formed were collected and air dried (yield = 35%). The infrared spectrum (Figure 3) showed

asymmetric and symmetric carboxylate absorption bands at 1580 and 1415, respectively.⁽⁵⁾ The TGA indicated that 98% of the compound would sublime (MP 232°C). The mass spectrum also agreed with the proposed dimeric structure.

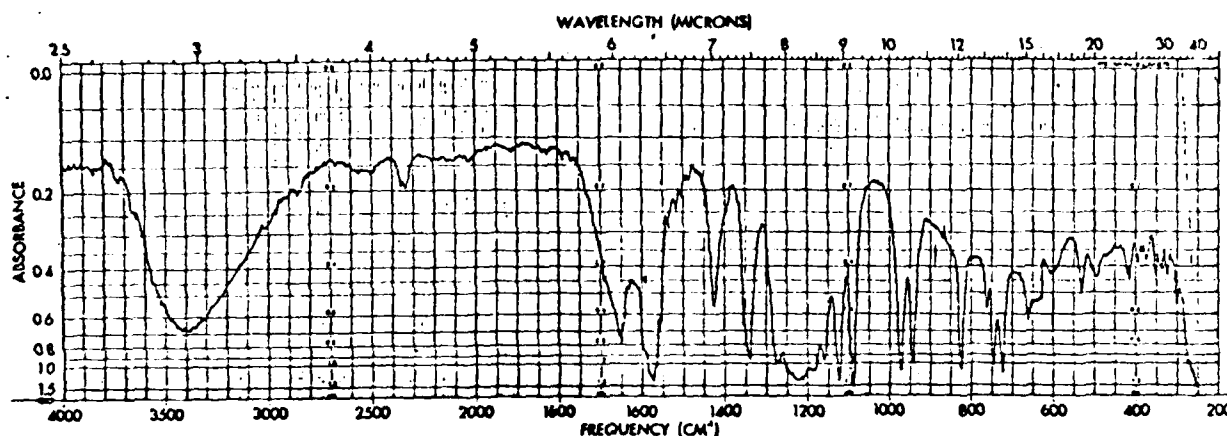


Figure 3. Infrared Spectrum of Molybdenum(II) Heptafluorobutyrate.

(8) Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)-molybdenum(IV) dichloride

A 0.03-mole sample of H(thd) was added to 0.01 mole of MoCl_5 and heated to 120°C. Hydrogen chloride was evolved immediately. The product was extracted with hot CCl_4 to give a blue solid.⁽⁶⁾

b. Results and Discussion

Molybdate is peculiar in its behavior. Several isopolymolybdates are known to exist under different pH conditions and transitions from one species to another are never abrupt. The paramolybdates are stable between pH 1 and 4.5, and below pH 2.24 an appreciable concentration of MoO_2^{++} is in equilibrium with the main aggregate $\text{Mo}_7\text{O}_{24}^{-6}$ ion. At pH 8.1-8.9 the ion in solution is mainly MoO_4^{-2} . An aqueous solution of 2-ethylhexylamine will have a pH of approximately 9; therefore,

the proposed stoichiometry of the isolated product is $[\text{C}_8\text{H}_{17}\text{NH}_3]_2 \text{MoO}_4 \cdot \text{H}_2\text{O}$. The presence of one water is substantiated by the elemental analysis and the absorption at 3500-3400 cm^{-1} in the infrared spectrum (Figure 1).

Several dioxomolybdenum compounds were prepared to determine if this class of compound possesses the necessary stability for use as a standard. The synthesis of the thd derivative has not been reported in the literature. The thd derivative was synthesized from the acetylacetonate derivative and tentatively characterized by its infrared spectrum. The infrared spectrum (Figure 2b) shows M=O stretching modes in the 900 cm^{-1} region as expected for a bent MoO_2 group (Table 2).

TABLE 2
ABSORPTION OF INFRARED RADIATION BY THE MoO_2 GROUP

Compound	Media	Sym Mo=O	Antisym Mo=O
$\text{O}_2\text{Mo}(\text{AcAc})_2$	Nujol	943	915
$\text{O}_2\text{Mo}(\text{thd})_2$	Nujol	948	920
$\text{O}_2\text{Mo}(\text{oxinate})_2$	Nujol	930	905

The oxinate (8-quinolinolate) was also prepared from the acetylacetonate derivative. Both $\text{O}_2\text{Mo}(\text{AcAc})_2$ and $\text{O}_2\text{Mo}(\text{oxinate})_2$ are unstable in the solid state and were not evaluated further. The thd derivative is stable in the solid state and is soluble in ester base oils. However, a small sample dissolved in ester oil decomposed and precipitated as a white powder within one day; but a sample stabilized with 2-ethylhexanoic acid and 6-methylheptanedione was stable in ester oil.

The molybdenum(II) carboxylates are reported to be dimeric with molybdenum-molybdenum quadrupole bonds. The heptafluorobutyrate was prepared by Stephenson et.al.⁽⁵⁾ and was

their most stable molybdenum carboxylate. The molybdenum heptafluorobutyrate was dissolved in ester oil but was unstable in solution. However, adding heptafluorobutyric acid to the oil stabilized the solution.

The molybdenum compound, $O_2Mo(thd)_2$, was evaluated as a possible molybdenum standard. This compound was solubilized with 2-ethylhexanoic acid and diluted with MIL-7808 ester oil. After 72 hours a precipitate was observed at concentrations less than 100 ppm. A stable solution was obtained by adding 5% H(thd) to the ester oil. Also, preliminary tests indicate that $O_2Mo(thd)_2$ and $Pb(thd)_2$ are not compatible. When ester oil solutions of the two compounds are mixed, a precipitate is observed which cannot be prevented by the addition of H(thd). The use of $O_2Mo(thd)_2$ as a standard is reported in Section III which describes the T12 (thd) standards.

Preliminary results have been obtained on the use of MoO_3 and $Mo(CO)_6$ as molybdenum standards. The analytical results (Figure 4) show that $Mo(CO)_6$ gave results that are higher than Conostan aryl alkyl sulfonates while MoO_3 gave results similar to Conostan standards. The MoO_3 and $Mo(CO)_6$ standard solutions are stable in ester oils for at least 1 year.

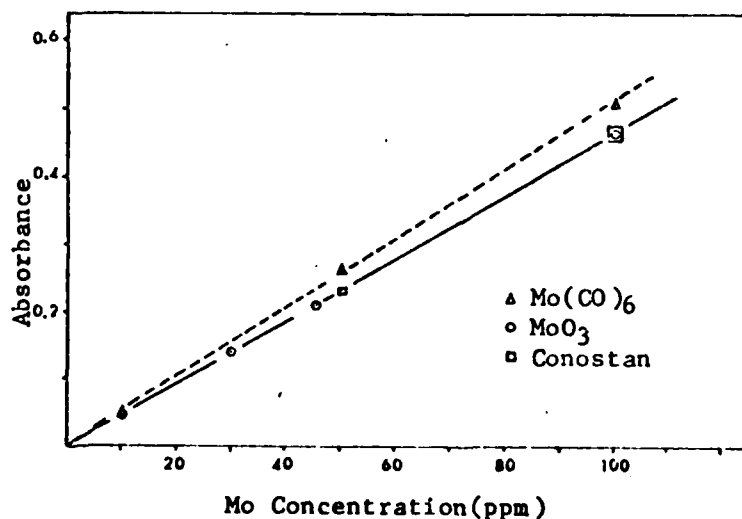
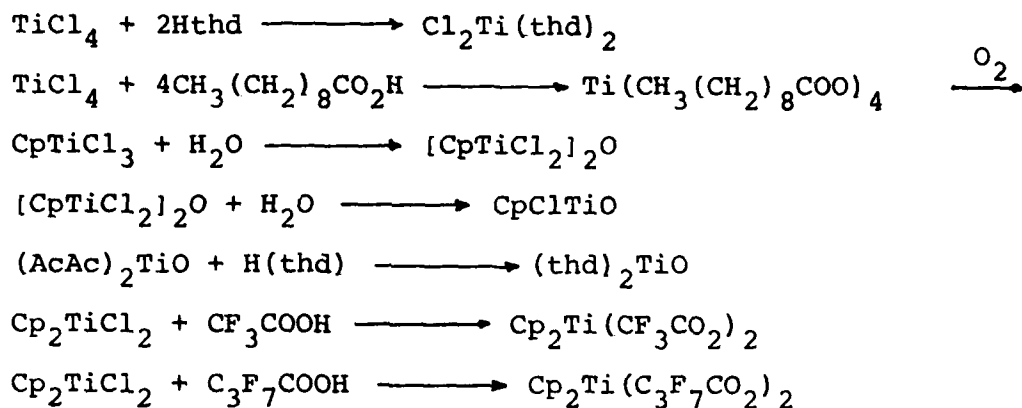


Figure 4. AA Analysis of Mo Standards

2. DEVELOPMENT OF AN ORGANOMETALLIC TITANIUM STANDARD

Research was carried out to develop a stable, oil soluble titanium compound for use as a standard in the Spectrometric Oil Analysis Program. Table 3 lists some of the reactions investigated.

TABLE 3
SYNTHESIS OF ORGANOMETALLIC TITANIUM COMPOUNDS



a. Experimental

- (1) Bis(2,2,6,6-tetramethyl-3,5-heptanedionato) titanium (IV)dichloride

A 0.01-mole sample of titanium tetrachloride was added to 40 ml of anhydrous benzene in an Erlenmeyer flask. A 0.03-mole sample of H(thd) was added slowly to the benzene solution resulting in the evolution of hydrogen chloride. After the addition of H(thd) was completed, the solution was heated overnight at 60°C. The volume of the reaction mixture was reduced to 25 ml and then cooled to room temperature. Red orange crystals formed which were isolated by filtration. The melting point of the product was 134-142°C. Attempts to recrystallize the product resulted in decomposition to a yellow oil. The

infrared spectrum (Figure 5) showed typical thd and Ti-Cl bands. Elemental analysis gave:

Obs.	8.3% Ti	55.3%C	7.95%H	14.65% Cl
Calc.	8.3% Ti	54.4%C	7.8%H	14.6% Cl

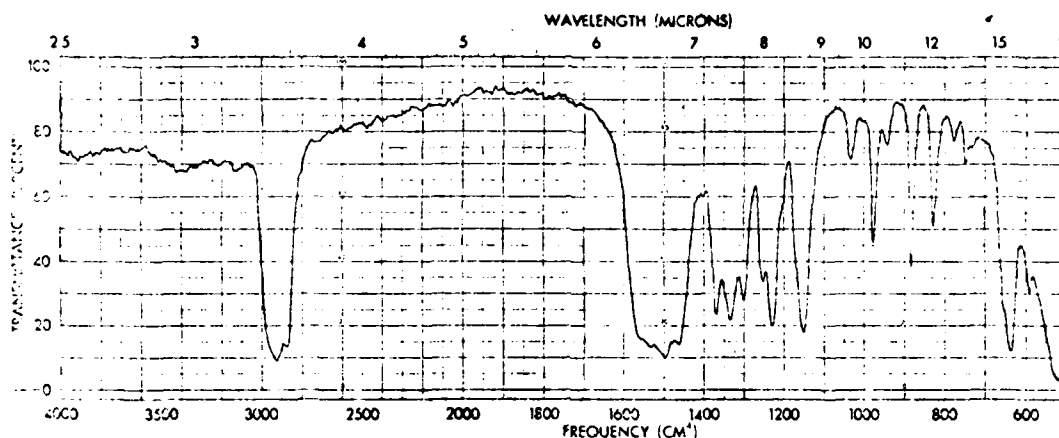


Figure 5. Infrared Spectrum of $(\text{thd})_2\text{TiCl}_2$ (Nujol)

(2) Reaction of Titanium Tetrachloride with Capric Acid

A 0.4-mole sample of capric acid was dissolved in 50 ml heptane. A 0.1-mole sample of titanium tetrachloride was dissolved in 50 ml heptane and the resulting solution was added slowly to the capric acid solution. Hydrogen chloride was evolved and the reaction mixture was heated at 80°C for several days. The heptane was evaporated and a dark brown liquid remained. This dark liquid solidified when cooled to give a compound which analyzed for $\text{Ti}(\text{caprate})_4 \cdot \text{capric acid}$.

Obs.	5.5% Ti	66.6%C	11.00%H
Calc.	5.3% Ti	66.4%C	10.6%H

(3) Bis(cyclopentadienyldichlorotitanium(IV)oxide

A 0.1 g. sample of CpTiCl_3 was dissolved in heptane and heated to boiling in an open beaker for 10 minutes. The heptane was evaporated and the yellow solid collected by

filtration to give $[\text{CpTiCl}_2]_2\text{O}$ (MP 148-150°C; Lit. MP 145-150°C).⁽⁷⁾

(4) Cyclopentadienylchlorotitanium(IV) oxide

A 0.1-g sample of CpTiCl_3 was dissolved in 20 ml of xylene saturated with H_2O at 20°C. The resulting solution was heated to boiling for two minutes, then cooled to room temperature, and the xylene allowed to evaporate overnight to give CpTiClO (MP d 255°C; Lit. d 258-260°C).⁽⁷⁾

(5) Bis(2,2,6,6-tetramethyl-3,5-heptanedionato) titanium(IV) oxide

A 2.6-g sample of $(\text{AcAc})_2\text{TiO}$ was placed in a beaker and 4.0 g of $\text{H}(\text{thd})$ was added. The reaction mixture was heated at 100°C for 48 hrs. Approximately 50 ml of hot benzene was added to the reaction mixture and the mixture was filtered. The crystals which formed in the filtrate were isolated and purified by recrystallization from heptane. The infrared spectrum is indicative of $(\text{thd})_2\text{TiO}_2$ (Figure 6). The compound decomposed at about 300°C without melting.

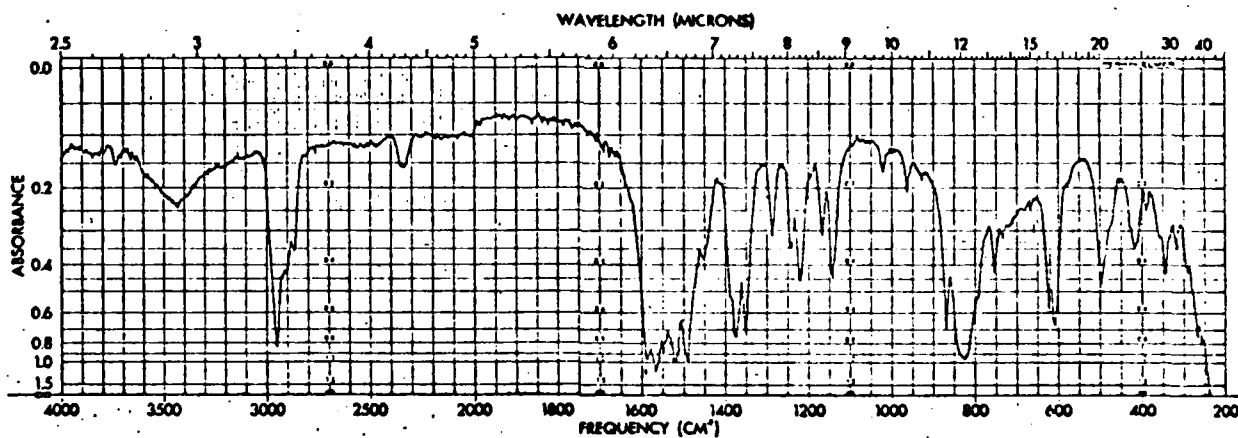


Figure 6. Infrared Spectrum of $(\text{thd})_2\text{TiO}$

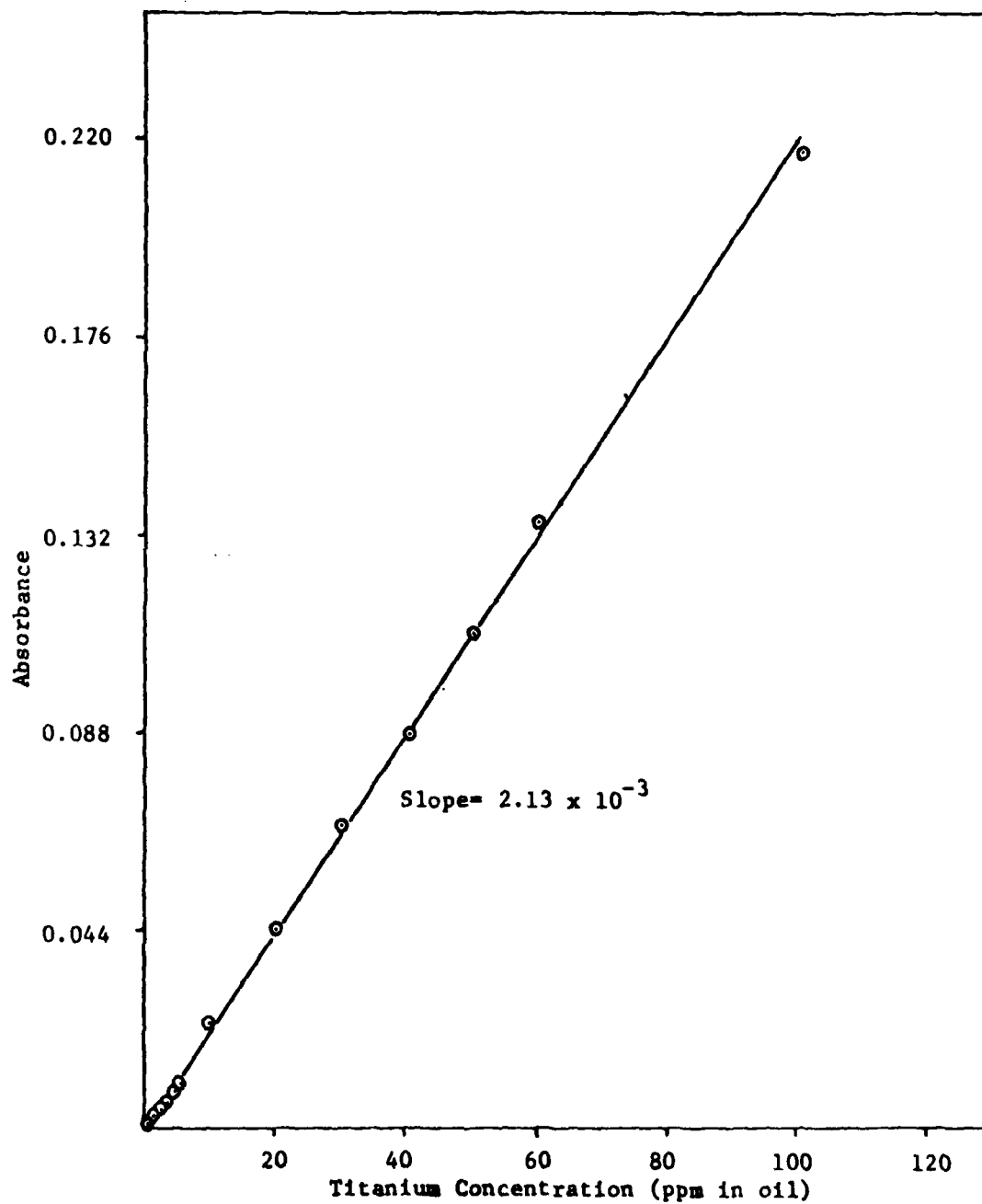


Figure 7. Plot of Absorbance vs. Titanium Concentration

(6) Ti Standard from $(\text{thd})_2\text{TiCl}_2$

A 0.5062g sample of $(\text{thd})_2\text{TiCl}_2$ was dissolved in a mixture of 2 g 2-ethylhexanoic acid, 0.5 g xylene and 1 g 2,2,5,6-tetramethylheptanedione ($\text{H}(\text{thd})$). This solution was then diluted with Mobil MIL-L-7808H oil to obtain 50 g of a solution containing 1000 ppm Ti. Different quantities of this solution were diluted with Mobil ester oil to give standard solutions of 100 and 40 ppm Ti.

(7) Ti Standard from Cp_2TiCl_2

A 0.5187-g sample of Cp_2TiCl_2 , which had been recrystallized from methylene chloride, was dissolved in a mixture of 2.5 g 2-ethylhexanoic acid, 1 g xylene, 1 g 2-ethylhexylamine, and 1 g 6-methylheptanedione. This solution was then diluted with Mobil ester oil (MIL-7808) to obtain 100 g of a solution containing 1000 ppm Ti. Different quantities of this solution were diluted with Mobil ester oil to give standard solutions of 100 and 50 ppm Ti.

(8) Ti Standard from Ti Powder

A 53.14-mg sample of 325 mesh (44 microns) titanium powder, obtained from Metal Hydrides Co., was suspended in blank oil to prepare 265.7 grams of a 200 ppm Ti solution. One milliliter of an acid solution, prepared from 1 ml concentrated HF and 3 ml concentrated HCl, was added to the oil mixture and then shaken vigorously for five minutes (in order to oxidize all Ti powder in the oil). Aliquots of this solution were diluted with two parts MIBK by weight to prepare a series of solutions containing 1-100 ppm Ti. The results of the AA analyses are illustrated in Figure 7.

b. Results and Discussion

A 0.068-gram sample of the reaction product isolated from the reaction of titanium tetrachloride and capric acid was dissolved in ester oil to evaluate the compound for

stability. This product has not been totally characterized but the analysis indicates that a possible structure is $\text{Ti}(\text{caprate})_4 \cdot \text{HO}_2\text{C}(\text{CH}_2)_8\text{CH}_3$. The agreement between calculated and experimental C,H data may be fortuitous, and not enough information regarding the molecular formula of this compound has been formulated at this time. The ester oil solution showed no signs of decomposition during a six month period.

Bis(2,2,6,6-tetramethyl-3,5heptanedionato)titanium(IV) dichloride and bis(cyclopentadienyl)-2,2,6,6-tetramethyl-3,5 heptanedianato titanium (IV) chloride were unstable in ester oils. Bis(acetylacetonate) titanium oxide was dissolved in H(thd) and diluted with ester oil and MIBK and evaluated for stability. This solution also showed significant (30%) decomposition after 30 days.

Preliminary results have been obtained on the use of $(\text{thd})_2\text{TiCl}_2$ and Cp_2TiCl_2 as titanium standards. The standard solutions were prepared and stabilized as presented in the experimental section. The analytical results (Figure 8) show that these compounds are potential standards for Ti. After six months these compounds showed only slight decomposition.

The compound $(\text{thd})_2\text{TiO}$ shows promise as a titanium standard. This compound can be recrystallized from heptane and is soluble and stable in ester oil using 2-ethylhexanoic acid as a stabilizer. The use of $(\text{thd})_2\text{TiO}$ as a standard is reported in Section III which describes the T12 (thd) standards.

3. METAL CAPRATES

The British⁽⁸⁾ have proposed that the metal salts of capric acid $(\text{CH}_3(\text{CH}_2)_8\text{COOH})$ merit consideration as analytical standards. The metal caprates are not soluble in oils but may be solubilized with naphthenic acid or they may be used in place of metal cyclohexanebutyrates in the preparation of OAP

standards by the NBS solubilization procedures. The metal caprates were synthesized to evaluate them as possible alternative standards for Air Force applications.

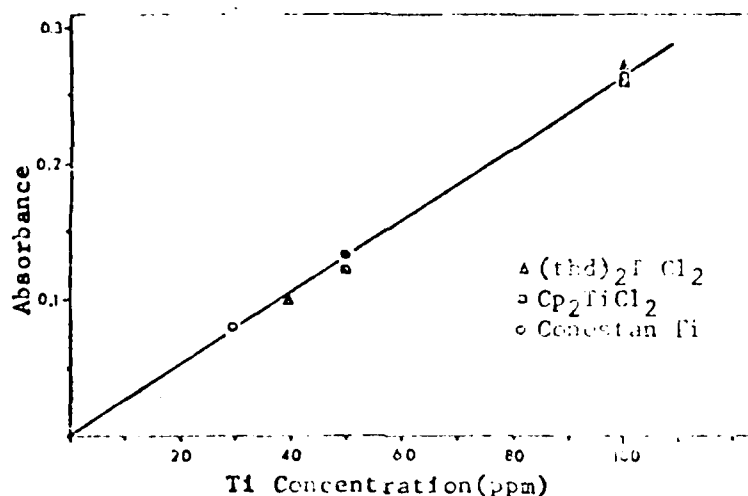


Figure 8. AA Analysis of Ti Standards

a. Experimental

The metal caprates were prepared by published methods.⁽⁸⁾ For example, 250 ml of 1 M ammonium caprate was diluted with water and an aqueous solution of the metal salt (26 grams $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) was added. The resulting precipitate was collected by filtration with a Buchner type glass funnel. The product was washed with water several times and then with acetone. The metal caprate was then air-dried, powdered, and finally dried in vacuo over P_2O_5 . The caprates prepared are listed in Table 4 along with the elemental analysis results.

b. Results and Discussion

The results from the analyses of the metal caprates were satisfactory. The percentage of metal in some of the metal caprates did not agree with the values reported by Hearn, Mostyn and Bedford.⁽⁸⁾ Therefore, an attempt was made to purify the caprates by washing each compound five times with

300-500 ml distilled water followed by three washings with 150 ml of acetone. The iron caprate was not washed with acetone because it is partially soluble in this solvent. The metal caprates were all air-dried and macerated. The caprates of Cu, Ni, Cr, Al and Mg were further dried at 100-110° in vacuo for 24 hours. The caprates of Ag, Pb and Fe were dried in vacuo over P₂O₅ at room temperature, due to their low melting or thermal decomposition points.

Further characterization of the metal caprates was attempted in order to determine their purity and empirical formulas. Table 5 lists the melting points of the caprates. The melting points were difficult to define since the compounds would soften at a relatively low temperature and then melt over rather large temperature ranges. Most of the caprates melted to give viscous liquids. It is apparent that the melting points will not be good indicators of purity.

The metal caprates are generally soluble in amines, such as 2-ethylhexylamine and pyridine, in ethers such as tetrahydrofuran and in acids such as acetic acid and 2-ethylhexanoic acid. In addition to the above solvents, the iron and copper caprates are partially soluble in acetone and MIBK, respectively. Lead caprate is an exception and is soluble only in 2-ethylhexanoic acid. Although the metal caprates are soluble in these solvents, they are not amenable to purification by recrystallization in any solvent system studied to date.

Infrared spectra of the metal caprates were taken at various times during attempts to purify these compounds. The infrared spectra were found to be useful in detecting the presence of unreacted capric acid by the presence of the C=O absorption band for capric acid at 1700 cm⁻¹ (Figure 9). The spectra were also of value in determining dryness and the relative purity of each metal caprate.

TABLE 4
ELEMENTAL ANALYSIS OF METAL CAPRATES

	%C		%H		%M	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
Ag(caprate)	42.9	43.03	6.8	6.86	38.7	38.67
Cu(caprate) ₂	54.6	59.2	8.9	9.43	15.3	15.67
Ni(caprate) ₂	56.2	59.87	9.72	9.55	13.7	14.63
Cr(caprate) ₂ OH	58.8	58.36	9.47	9.50	14.2	12.63
Fe(caprate) ₃	61.4	63.26	10.0	10.09	9.6	9.8
Pb(caprate) ₂	42.5	43.7	6.75	6.9	37.2	37.7
Al(caprate) ₂ OH	62.6	62.6	10.2	10.1	6.5	6.99
Mg(caprate) ₂	65.2	65.48	10.5	10.44	5.2	6.63

TABLE 5
MELTING POINTS OF METAL CAPRATES

Compound	M.P. °C	
Pd(caprate) ₂	94-107	
Ag(caprate)	d<250	gradually became brown decomposing prior to 250°C
Cr(caprate) ₂ OH	197-210	
Fe(caprate) ₃	61-70	gradually melted to become a viscous dark brown oil
Cu(caprate) ₂	257-258	
Mg(caprate) ₂	162-165	
Ni(caprate) ₂	>250	never melted
Al(caprate) ₂ OH	190-195	

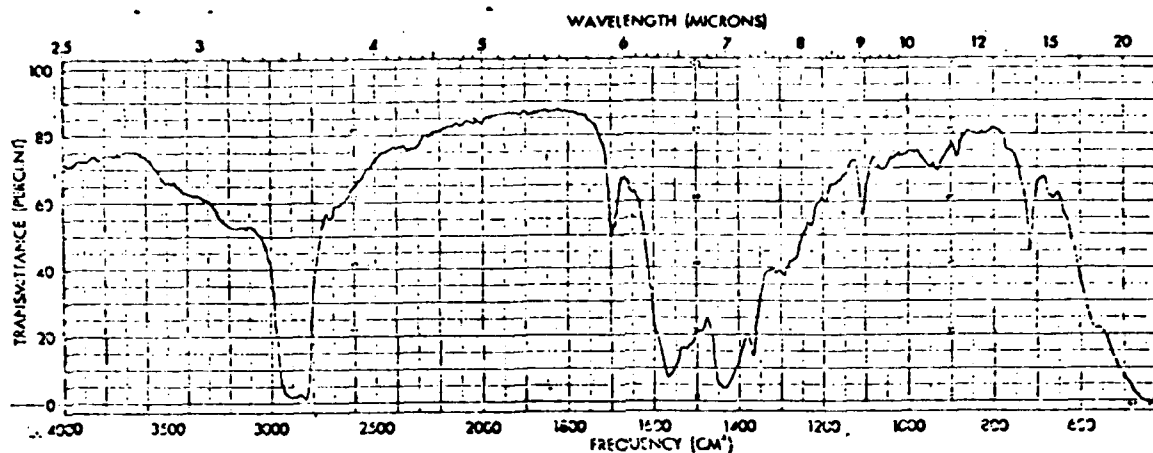


Figure 9. Infrared Spectrum of Impure Iron Caprate (Nujol)

Table 6 lists the antisymmetric and the symmetric C=O stretching frequencies for the metal caprates. Their energy difference, ΔE , is a useful parameter for examining bonding to carboxylate groups.⁽⁹⁾ A large ΔE value is considered to be due to an asymmetric carboxylate metal complex, $-\text{CO}_2-\text{M}$, $-\text{C} \begin{smallmatrix} \text{O} \cdots \text{M} \\ \diagdown \quad \diagup \\ \text{O} \end{smallmatrix}$ or $-\text{C} \begin{smallmatrix} \text{O} \cdots \text{M} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}$. Multiple absorption bands in the carboxylate region indicate the presence of two types of carboxylate ions.

The infrared spectra of hydrated and dried copper caprate are shown in Figure 10. The presence of water gives rise to additional C=O bands similar to those observed for $\text{Cu}(\text{benzoate})_2 \cdot 3\text{H}_2\text{O}$ ⁽⁹⁾ which has the structural formula $[\text{Cu}(\text{H}_2\text{O})_2 \text{ benzoate}]_n (\text{H}_2\text{O} \cdot \text{benzoate})_n$. A similar structure is possible for the hydrated copper caprate where different absorption bands are observed for the two possible carboxylate types.

TABLE 6
CARBOXYLATE ANTISYMMETRIC AND SYMMETRIC
STRETCHING FREQUENCIES

<u>Compound</u>	<u>C=O Anti</u>	<u>C=O Sym</u>	<u>ΔE</u>
Pb(cprate) ₂	1515	1425	90
Ag(caprate)	1520	1430	85
Cr(caprate) ₂ OH	1540	1415	125
*Fe(caprate) ₃	1585(1565)	1430	155(135)
Cu(caprate) ₂	1585	1415	170
Mg(caprate) ₂	1540	1410	130
Ni(caprate) ₂	1565	1425	140
Al(caprate) ₂ OH	1570	1425	145
Na(acetate)	1560	1445	115
Cu(acetate) ₂	1600	1425	175

* Multiple carboxylate absorption bands present

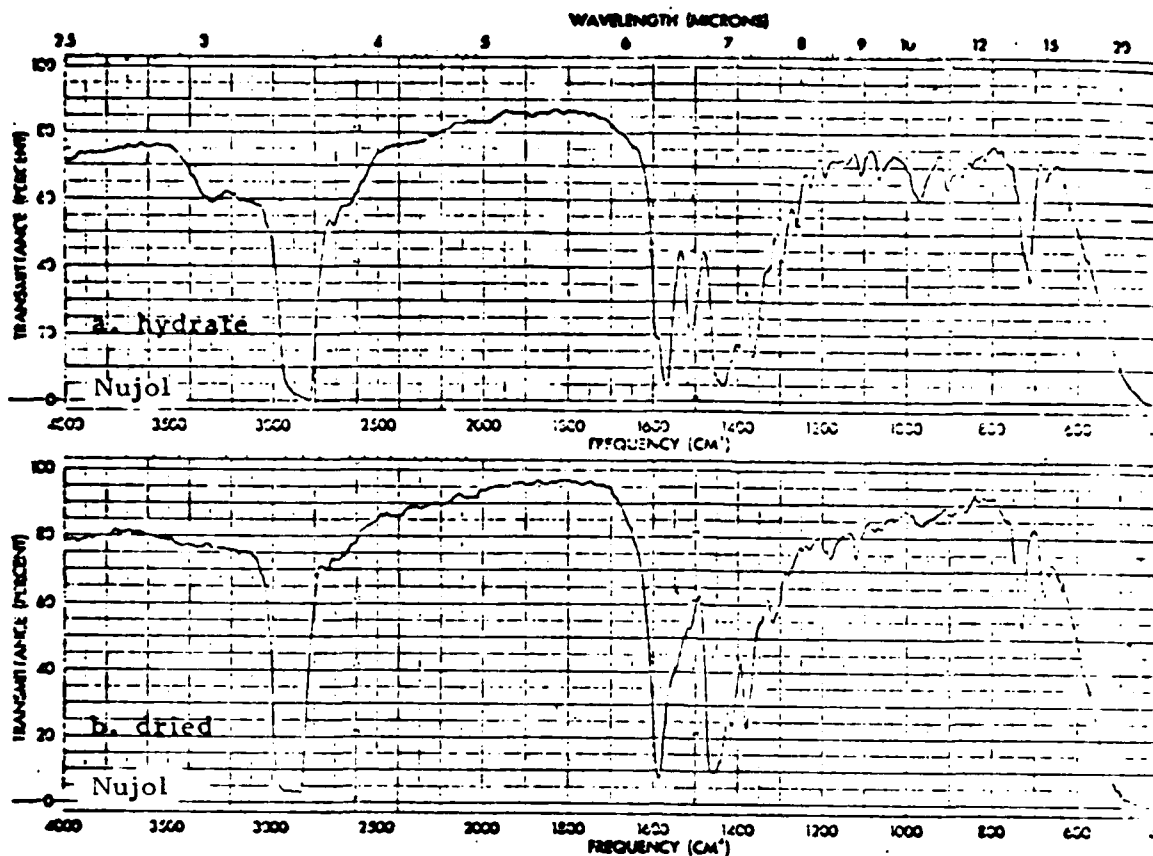


Figure 10. Infrared Spectra of Cu Caprates

The infrared spectrum of chromium caprate shows evidence of OH groups and the carbon hydrogen percentages agree best with a formula of $\text{Cr}(\text{caprate})_2\text{OH}$ or $[\text{OCr}(\text{caprate})_2]_3\text{OH}$. The latter formula was shown to be the structure of basic chromium acetate by a single crystal x-ray structure determination. (10)

The absorption band at 3700 cm^{-1} in the infrared spectrum of aluminum caprate along with the band at 990 cm^{-1} are interpreted as evidence that aluminum caprate is also a hydroxide, $\text{Al}(\text{caprate})_2\text{OH}$, or a basic carboxylate. Not enough information is known at this time to propose exact structural

formulas for aluminum and chromium caprates.

Thermogravimetric analysis (TGA) was also employed to analyze the caprates of Cr, Al and Fe, since these caprates are possibly similar and their stoichiometries the most difficult to determine. Chromium caprate is the most stable, having lost one-half of its weight (1/2 wt) at 480°C in a N₂ atmosphere while aluminum caprate reached 1/2 wt at 340°C. Iron caprate is the least stable, having reached 1/2 wt at 390°C. Based on the assumption that the metal oxide is formed, we calculated the following metal percentages: 6.4% Al, 10.7% Fe and 12.4% Cr. These percentages agree with those determined by Materials Lab Analytical Services.

Atomic absorption studies of the caprates are reported in Section III. The metal caprates were solubilized in approximately three grams of p-xylene and three grams of 2-ethylhexylamine, except lead caprate which was dissolved in p-xylene and 2-ethylhexanoic acid. The solubilized samples were then dissolved in ester oil and diluted 1:2 with MIBK. The silver caprate solution turned brown over a four-day period while setting in room light.

4. METAL 2-ETHYLHEXANOATES

Several metal 2-ethylhexanoates were prepared in order to evaluate: (1) the increase or decrease in solubility and stability by branching and shortening of the alkyl group; and (2) the claim by NBS⁽¹¹⁾ that these compounds are mostly oils and more difficult to isolate and purify than other metal carboxylates.

a. Experimental

(1) Potassium 2-ethylhexanoate

The 2-ethylhexanoic acid was converted to the potassium salt by dissolving 0.5 mole potassium hydroxide in

water and transferring to a 500-ml volumetric flask. A 0.5-mole sample of 2-ethylhexanoic acid was added to the above solution and the mixture was diluted to 500 ml with water.

(2) Bis(2-ethylhexanoate)copper(II)

A 0.025-mole (25 ml) sample of the potassium acid salt solution was placed in a beaker, and a 0.0125-mole sample of $\text{Cu}(\text{NO}_3)_2$ dissolved in water was added slowly with stirring. A blue-green precipitate formed which was isolated by filtration and then air dried. The product is soluble in heptane but does not recrystallize nicely from this solvent. Figure 11a, shows the infrared spectrum. A pyridine adduct was obtained by adding pyridine to a heptane solution of the copper compound. The pyridine adduct is extremely soluble in hydrocarbons such as heptane and will not form a solid compound until all the heptane has been evaporated. The infrared spectrum is shown in Figure 11b.

(3) Bis(2-ethylhexanoate)nickel(II)

A 0.0125-mole sample of nickel(II) acetate was dissolved in 20 ml of water and slowly added to 25 ml of the potassium 2-ethylhexanoate solution. A green sticky precipitate formed which could be isolated by decanting off the water or extracting into heptane. A green non-crystalline viscous oil was isolated. The infrared spectrum indicates unreacted acid may be present (Figure 11c). The infrared spectrum of the neat compound was obtained by dissolving the compound in heptane and evaporating the solution on NaCl plates to obtain a thin film suitable for infrared analysis.

A pyridine adduct was obtained by adding pyridine to a heptane solution of the green oil. As pyridine was added, the solution turned from green to blue and a crystalline product was isolated as the heptane evaporated. The infrared spectrum is shown in Figure 11d.

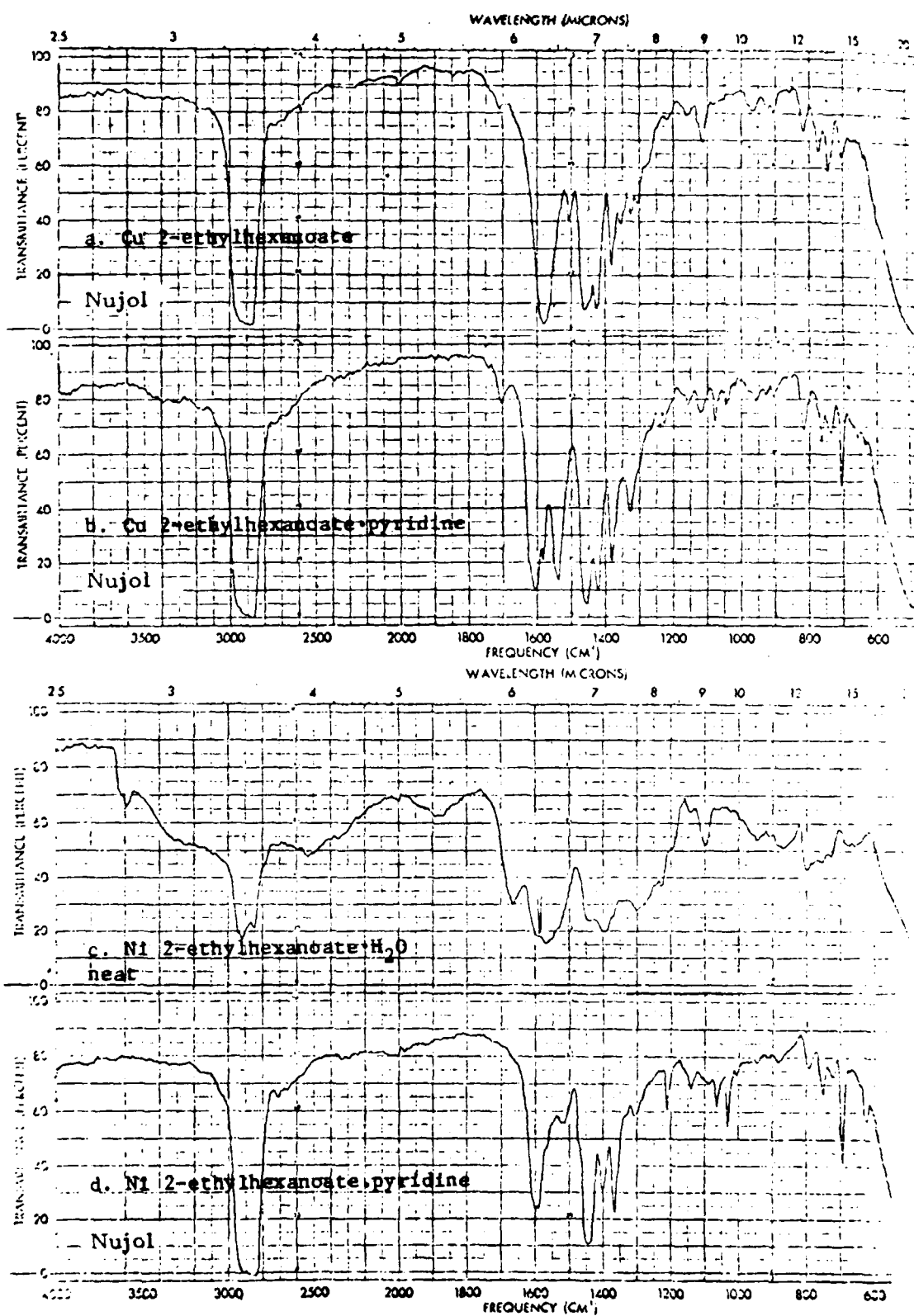


Figure 11. Infrared Spectra of Copper and Nickel 2-Ethylhexanoates

(4) Bis(2-ethylhexanoate) chromium(III)hydroxide or basic chromium 2-ethylhexanoate

A 0.025-mole sample of the potassium 2-ethylhexanoate was placed in a beaker and a 0.008-mole sample of CrCl_3 dissolved in water was added. A viscous oil formed which was extracted into heptane to give a dark purple solution. The heptane solution became cloudy [$\text{Cr}(\text{OH})_3$] and was filtered with difficulty to give a clear purple solution. After evaporation of the heptane, a purple oil remained. The product was washed with several portions of acetone and the resulting purple powder was isolated by filtration and air-dried. The infrared spectrum has bands at 3600 and 910 cm^{-1} (neat film).

(5) Bis(2-ethylhexanoate)iron(III)hydroxide

A 0.008-mole sample of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in water and added to 25 ml of 1 M potassium 2-ethylhexanoate solution to give a red oil. The product was extracted into heptane, dried over MgSO_4 , and the heptane evaporated to give a viscous oil. The product was only partially soluble in methanol and the insoluble portion was isolated by filtration. The isolated solid was soluble in benzene and showed absorption bands at 3600 cm^{-1} and 845 cm^{-1} in the infrared spectrum (neat film). The methanol soluble portion has not been identified at this time.

b. Results and Discussion

The preliminary results obtained on the 2-ethylhexanoic acid metal complexes are promising. These compounds show good solubility in hydrocarbon solvents and only the iron compound proved to be difficult to purify and isolate. The isolation of a crystalline pyridine adduct of the nickel compound is also encouraging.

The infrared spectra of the Fe, Cr, and Al 2-ethylhexanoates indicate that these compounds have similar structures and have tentatively been assigned the formula $\text{HOM}(\text{C}_7\text{H}_5\text{COO})_2$.

The Al 2-ethylhexanoate was obtained from NBS.

5. METAL β -DIKETONATES

The 2,2,6,6-tetramethyl-3,5-heptanedionates (thd) listed in Table 7 were prepared⁽¹²⁾ to evaluate these chelates as possible candidates for oil analysis standards. These compounds were chosen since they are crystalline and easily purified materials. The iron 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate (fod) was also prepared for evaluation as a standard.⁽¹³⁾

a. Experimental

(1) Preparative Method A

A methanol solution of the tetramethylheptanedione (H(thd)) was added to an aqueous solution containing the metal salt (chloride or nitrate) and an excess of sodium acetate. The metal chelate was isolated by filtration.

TABLE 7
ELEMENTAL ANALYSES OF METAL β -DIKETONATES

	%C		%H		%M		%Cl	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
Ni(thd) ₂	62.23	62.22	9.06	9.02	13.16	13.80	12.6	12.75
Mg(thd) ₂	63.45	67.59	9.91	9.82	3.8	6.22		
Cu(thd) ₂	61.43	61.43	8.90	8.92	12.7	14.77		
Al(thd) ₃	68.20	68.70	9.78	9.98	4.3	4.68		
Cr(thd) ₃	65.6	65.85	9.25	9.56	8.7	8.64		
Fe(thd) ₃	65.49	65.43	9.25	9.50	8.4	9.22		
Fe(fod) ₃	38.7	38.26	3.27	3.27	4.8	5.95		
Sn(thd) ₂ Cl ₂	47.7	47.51	7.03	6.89	21.0	21.34	12.6	12.75

(2) Preparative Method B

The metallic chloride, acetate or nitrate was

dissolved in methanol and the H(thd) was added. Stoichiometric amounts of an aqueous potassium hydroxide solution was added dropwise while stirring. The metal chelate was isolated by filtration.

(3) Preparation of Metal Fods

Potassium fod was prepared by adding equimolar amounts of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione (H(fod)) and potassium hydroxide to 100 ml of diethylether. The metal salt (i.e. chloride or acetate), dissolved in a minimal amount of water, was added to the ether solution. The metal β -diketonate was then isolated from the ether layer using standard procedures. The β -diketonates were purified by sublimation.

(4) Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)-magnesium(II)

The magnesium chelate was prepared by heating a solution of H(thd) in 70% aqueous ethanol under reflux in the presence of metallic magnesium. The chelate crystallized from the reaction mixture on cooling and was purified by recrystallizing from heptane. One sample melted at 94°C and another at 136°-139°C (two preparations). An attempt to sublime the sample which melted at 94°C resulted in decomposition. The infrared spectrum of (thd)₂Mg shows an absorption band at 3600 cm⁻¹ indicating the presence of H₂O. Recrystallization of (thd)₂Mg from pyridine gave a compound which has a melting point of 148°-154°C. These compounds have not been fully characterized.

(5) Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)-chromium(III)

The chromium chelate was prepared by dissolving 3 g CrCl₃·6H₂O, 5 g H(thd) and 5 g triethylamine in DMF. The reaction mixture was heated for several days and the precipitate was filtered and sublimed in vacuo to yield dark purple

crystals with a melting point of 229-231°C.

(6) Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)tin(IV) dichloride

Bis(tetramethylheptanedionato)tin(IV) dichloride was prepared by dissolving 0.01 mole of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in methanol and adding 3.7 g (0.02 mole) of H(thd). The reaction mixture was heated for several hours and allowed to set overnight. The next day the solid residue was extracted with heptane and filtered. Only a small amount was not soluble in heptane. Clear large crystals were obtained from the heptane solution. The melting point of the product was 115-117°C.

(7) (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)silver(I)

A 0.01-mole sample of H(fod) and 0.01-mole sample of NaOAc were dissolved in ethanol which contained just enough water to dissolve the NaOAc. This solution was added to 0.01 mole AgNO_3 dissolved in 20 ml water. A fine white precipitate formed which was isolated by filtration. The solid turned brown upon exposure to light. The Ag(fod) decomposed at 160°C.

b. Results and Discussion

Tetramethylheptanedione derivatives of all wear metals except Si and Ag have been prepared. All indications are that these compounds would make good standards for wear metal analysis. The magnesium derivative prepared does not have the same physical properties as the compound described in the literature. The infrared spectrum of this compound indicates that H_2O may be present.

The fluorinated β -diketones were also prepared. Pure fod's of Fe, Al, Pb and Cu were obtained by sublimation. The physical properties of the β -diketonates are given in Table 8.

The thd and fod derivatives were tested for solubility and stability in Mobil MIL-L-7808H ester oil (Table 9). Only

TABLE 8
PHYSICAL PROPERTIES OF METAL β -DIKETONATES

	Method of Preparation	Method of Purification	Color	M.P. °C	Lit M.P. °C	Lit Ref
Ni(thd) ₂	A, B	sublimation	pink	223-225	225	12
Cu(thd) ₂	A, B	sublimation	blue	195-196	198	12
Mg(thd) ₂		recryst from ethanol	white	136	60	31
Cr(thd) ₃		sublimation	purple	229-231	99, 136	12
Al(thd) ₃	A, B	recryst from heptane	white	263-265	229	12
					264	12
Fe(thd) ₃	A, B	sublimation	red	164-165	163	12
Sn(thd) ₂ Cl ₂		recryst from heptane	colorless	115-117		
Ti(thd) ₂ Cl ₂		recryst from heptane	orange	134-142		
Mo(thd) ₂ O ₂			light green	131-133		
Pb(thd) ₂		sublimation	white	126-130	123	32
Ag(fod)			white	160		
Fe(fod) ₃		recryst from heptane	red	72-75	73-75	13
Cu(fod) ₂		sublimation	blue	66-67		
Ni(fod) ₂		sublimation	green	170-180		
Pb(fod) ₂		sublimation	white	76-80		
Mg(fod) ₂		sublimation	white	120		
Al(fod) ₃		sublimation	white	127.5-129		

TABLE 9
SOLUBILIZATION OF THD AND FOD DERIVATIVES
IN MOBIL MIL-L-7808H ESTER OIL

<u>Compound</u>	<u>Solubilizers</u>
Fe(thd) ₃	A*
Al(thd) ₃	None
Cr(thd) ₃	None
Ni(thd) ₂	A
Cu(thd) ₂	A
Sn(thd) ₂ Cl ₂	A
Pb(thd) ₂	A & B*
Fe(fod) ₃	None
Cu(fod) ₂	B
Pb(fod) ₂	None
Ni(fod) ₂	None
Mg(fod) ₂	A & B

*A = 2-ethylhexanoic acid

**B = 6-methylheptanedione

five of the compounds were stable when dissolved directly in the ester oil. But stable solutions of the other compounds were produced by first dissolving them in solubilizers and then diluting the solutions with Mobil ester oil.

The Al, Fe, Cr, Ni, Cu and Sn thd derivatives were also tested for solubility in di(2-ethylhexyl) sebacate and Phillips Condor 105. All the solutions were stable except $\text{Sn(thd)}_2\text{Cl}_2$ in the Condor 105.

6. METAL POWDERS

a. Introduction

The Spectrometric Oil Analysis Program (SOAP) is a diagnostic maintenance program used by the Air Force for monitoring the condition of aircraft engines. This program utilizes trace metal spectrophotometric techniques in order to monitor wear metal concentrations and recommend appropriate engine maintenance action. The spectrometric analyses of oil samples rely on calibration curves established with Conostan metallo-organic calibration standards. The advantages of using Conostan standards include high solubility in oil matrices, prolonged stability, and availability for twenty elements. However, these standards are only available from one supplier (Continental Oil Company, Conostan Division, Ponca City, Oklahoma), are expensive, and are quite chemically dissimilar to the wear metal particulates typically found in oil samples. The impact of using chemically dissimilar calibration standards for wear metal concentration measurements is discussed in Section IV.⁽¹⁹⁾ Alternative, less expensive and more available calibration standards have been studied and are discussed earlier in this Section. Finally, an important alternative to organometallic calibration standards is discussed in this subsection. This approach involves using high purity metal powders, suspended in oil, as oil calibration

standards. The results from this study are presented.

b. Experimental

(1) Preparation of Metal Powder Suspensions

Single element metal powder standards were prepared by direct weighing. Each metal powder standard was prepared in ester oil and the concentrations are given in Table 10. These metal powders were obtained from Atlantic Equipment Engineers, Bergenfield, N.J., and the purity of each powder was reported to be greater than 99 percent. The estimated particle sizes in each sample are also reported in Table 10.

In addition standards were prepared using a sedimentation procedure to remove the large particles. The large particles were allowed to settle out of the oil and the particles remaining in suspension were collected by decantation (Table 11). The concentrations isolated in the supernatant were determined by the particle size independent method.

The A/E35U-1 spectrometer (AE) was used for analyses of these suspensions. Twelve element Conostan standards in ester oil (C-12) were used to establish calibration curves. The reported AE concentrations were read directly from these curves. Atomic absorption (AA) analyses of the "As Received" metal powder standards required 1:2 (oil:methyl isobutyl ketone) dilution. Similarly, C12 standards were diluted and used to establish AA calibration curves. The concentrations reported were directly read from these curves.

(2) Ground Metal Powders

One-gram samples of Fe, Ti and Mo metal powders were sent to Micro Materials Corporation (MMC) Westbury, N.Y. to be ground on their Microjet 5 Spectromill. The ground powders received from MMC were submitted to AFML/LL for a particle size determination using a scanning electron

TABLE 10
PERCENT ANALYZABILITY OF "AS RECEIVED"
ATLANTIC EQUIPMENT ENGINEERS, INC. METAL POWDERS

Metal	Avg Particle Size (μ m)		AE (A/E35U-1) ^a			AA (PE 305B) ^b		
	As Reported by Source	SEM ^c	Calc. (ppm)	Found (ppm)	% Analyzability	Calc. (ppm)	Found (ppm)	% Analyzability
Cu	1 to 5	~10	100	0	0	332.2	0.1	0.03
Fe	1 to 5	~20	100	5.5	5.5	1373.1	10.9	0.79
Ni	<1	~5	200	16.0	8.0	8.4.0	2.0	0.25
Si	<1	10-20	100	6.5	6.5	150.0	0.7	0.47
Sn	1 to 5	~5	400	14.75	3.7	796.4	0.9	0.11
Ti	1 to 5	5-10				498.9	2.0	0.40
Mo	<1	0.5				899.3	0.6	0.07
Cr	<1	3	200	64	32	399.8		

^aThe Baird Atomic A/E35U-1 was calibrated using Conostan standard in ester oil (MIL-L-7808). Metal powders were also prepared in the same ester oil.

^bResults were obtained using the Conostan standard reference curve.

^cDetermined visually from Scanning Electron Microscope photograph.

TABLE 11
PERCENT ANALYZABILITY OF AEE
METAL POWDERS AFTER SEDIMENTATION

<u>Metal</u>	<u>Size Starting Material</u>	<u>Sedimentation Time</u>	<u>Calc. (ppm)</u>	<u>AE Found (ppm) *</u>	<u>% Analyzeability</u>
Cu	1-5 μ	3 hrs	40	17	43
Fe	1-5 μm	2 hrs	40	18	45
Ni	>1 μm	1 hr	60	10	17
Si	>1 μm	48 hrs	40	22.5	56
Sn	1-5 μm	24 hrs	60	18	30
Al	-325 Mesh	3 hrs	40	22	55
Cr	>1 μm	48 hrs	60	51	85
Mg	-325 Mesh	24 hrs	40	20	50

* Obtained from Research Organic/Inorganic Chemical Corporation
with reported purity > 99%

microscope (SEM) model AMR 900 and the Zeiss Particle Size Analyzer Model TGZ3. A small amount of each ground metal powder was suspended in methanol and shaken vigorously for one minute. Each suspension then set undisturbed (settling times reported in Table 12) before samples were withdrawn. The methanol suspensions were mixed with 5 g of ester oil in a one-ounce polyethylene bottle and diluted with 15 g of methyl isobutyl ketone. These samples were analyzed using AA according to Perkin-Elmer recommended procedures.⁽¹⁴⁾ These samples were also analyzed by AA after acid addition. The masses of methanol metal powder mixtures and the acid added are given in Table 12.

(3) Ultrafine Metal Powder Standards

Ultrafine metal powders were obtained from Vacuum Metallurgical Company (VMC), Shonan Building 1-14-10 Ginza Chuo-ku, Tokyo, Japan. The manufacturer reported sizes from 300Å to 2000Å average particle diameter.

The purity of these powders was determined using AA. Approximately 0.1 g of Ag, Ni, and Cu were dissolved in 8N HNO₃ and diluted with 1% HNO₃ to a final approximate metal concentration of 100 ug/ml. Approximately 0.1 g of Al, Sn, Cr and Mg were reacted and diluted with 6N HCl to 100 ug/ml. The Ni (1000Å) sample was heated to get complete dissolution. The Al sample reacted with HCl to give a yellow solution and a white precipitate. The Mg sample contained an impurity which was insoluble in HCl. Other samples of Al and Mg later received from VMC, reacted without forming insoluble material. Aqueous metal standards were similarly prepared from metal powders obtained from Research Organic/Research Inorganic Chemical Company. The concentrations of metal in the VMC samples were determined by AAS.

These VMC metal powders were then suspended in ester oil. The suspensions were diluted to give samples which were referred to as VMCl for single element suspensions and

TABLE 12
AA ANALYSES OF GROUND METAL POWDERS

<u>Metal</u>	<u>Time (min)^a</u>	<u>Weight (g)^b</u>	<u>Acid (6 drops)</u>	<u>AA Concentration Found (ppm)</u>	<u>Percent Analyzability</u>
Fe	1	0.3	--	1.2	
	1	0.3	6N H ₂ SO ₄	15.1	7.9
Mo	0	0.05	--	5.5	
	0	0.05	HF:HNO ₃ (1:3)	13.0	42.3
	3	0.3	--	62.1	
	3	0.3	HF:HNO ₃ (:3)	62.1	100.0
Ti	7	0.3	--	2.9	
	7	0.3	HF:HCl (1:3)	65.7	4.4

^aTime allowed for particles to settle after shaking

^bWeight of sample (metal powder + methanol)

VMC5 for suspensions of five elements. Conostan C-12 standards were used to establish AA and AE calibration curves. Samples analyzed using AA were diluted 1:2 (oil:methyl isobutyl ketone). The concentrations were directly read from the calibration curves. The Perkin-Elmer recommended analytical procedures⁽¹⁴⁾ were followed for AA determinations and Baird Atomic recommended procedures⁽¹⁵⁾ were used for the AE determinations.

Finally, settling rates of the VMC metal powders in ester oil were determined. The samples studied were VMC5 and VMCl-Sn. The VMCl-Sn was received after the studies on the VMC5 samples were completed. The samples set undisturbed and were analyzed at timed intervals, using the AE procedures recommended by Baird Atomic.⁽¹⁵⁾

a. Results and Discussion

The results for the Atlantic Equipment Engineer (AEE) metal powder suspensions are given in Table 10. These results show that directly weighed AEE metal powders give very poor recovery. Although the average particle sizes reported for each element were quite small, a large number of particles were found greater than the reported size. The contribution to the total weight of metal in these samples increases rapidly as the particle size increases. For example, in the case of spherical particles the mass of a particle increases as the cube of the particle diameter. Thus only a few large particles which cannot be detected spectrometrically will greatly reduce the analyzability of the metal powder sample.

Sedimentation was used to remove the large AEE metal particles from the oil suspensions. The analytical results for these samples are reported in Table 11. Although complete recovery of the metal in these samples was not observed, the percent analyzability for every metal increased dramatically.

The three metal powders which were ground by MMC were

expected to yield higher percent analyzabilities than the powder suspensions prepared with unground metal. The particle size distributions of Fe, Mo, and Ti ground powders are shown in Table 13. The conversion from volume percent to weight percent for Mo assumed particles were spherical while in fact these particles were not. Most of the particles in these samples were found, by volume distributions, to be less than 10 μm .

The analyses of these samples in oil are shown in Table 12. The ground metal powders were allowed to settle in methanol, a solvent which would prevent agglomerate formation of particles. The methanol/metal powder suspensions were mixed with oil and methyl isobutyl ketone prior to spectrometric analysis. Very good recovery was found for Mo, while Fe and Ti were slightly improved from the analysis results of sample prepared by directly weighing unground AEE metal powders. It was therefore concluded that grinding metal powders could not effectively produce metal powder calibration standards.

The metal powder samples obtained from VMC were reported by the manufacturer to have mean particle sizes ranging from 300 to 2000 \AA . The powders were produced by plasma vaporization and subsequent metal vapor condensation. Attempts to characterize these powders using SEM were not successful because the ultrafine particles were smaller than the resolution of the AFML/LL SEM.

Since these powders were extremely small and therefore extremely reactive, analyses to determine the purity of these metals were conducted. Two sets of samples were received and the second set of samples were of higher purity. The results of these analyses are given in Table 14. Some of the first metal samples received were contaminated with other metals and metal oxides. The cross-metal contamination was not evident with the second samples received. Although purity

TABLE 13

PARTICLE SIZE DISTRIBUTIONS FOR GROUND METAL POWDERS

Iron		Molybdenum			Titanium	
No. of Particles	Size (microns)	No. of Particles	Size (microns)	% Wt*	No. of Particles	Size (microns)
8	6.25	9	1.25	0.13	8	2.50
1	6.70	15	1.34	0.27	9	2.68
16	7.15	39	1.43	0.84	20	2.86
18	7.60	75	1.52	1.95	48	3.04
26	8.15	79	1.63	2.53	56	3.26
19	8.70	122	1.74	4.75	78	3.48
18	9.25	127	1.85	5.94	83	3.70
25	9.90	128	1.98	7.34	74	3.96
20	10.55	93	2.11	6.45	59	4.22
8	11.25	55	2.25	4.63	63	4.50
14	12.05	42	2.41	4.34	83	4.82
5	12.90	43	2.58	5.45	54	5.16
8	13.70	23	2.74	3.49	46	5.48
5	14.60	19	2.92	3.49	29	3.84
7	15.60	15	3.12	3.36	24	6.24
5	16.60	9	3.32	2.43	23	6.64
3	17.80	11	3.56	3.67	14	7.12
5	19.00	4	3.80	1.62	15	7.60
5	20.25	4	4.05	1.96	10	8.10
1	21.60	7	4.32	4.17	3	8.64
3	23.10	4	4.62	2.91	3	9.24
1	24.65	3	4.93	2.65	5	9.86
1	28.05	1	5.26	1.07	3	10.52
2	29.95	2	5.99	3.17	2	11.22
		1	6.39	1.93	1	11.98
		1	7.29	2.86	1	12.78
		3	7.78	10.43	1	16.60
		1	9.41	6.15		
Average Particle Size	11.04		2.09			4.50

$$* \% \text{ Wt} = \left\{ (\text{Number of particles})(\text{density})(4/3\pi r^3) / \text{Total wt} \right\} \times 100$$

check for lead was not conducted, it was visually observed to react, perhaps with oxygen, to form an oxidized lead compound. The metallic lead changed from a dark grey, the color of the lead powder as first received, to a tan.

The first set of metal powders received from VMC were suspended in ester oil and analyzed using AA and AE. The results are reported in Table 15. The calculated concentrations in this Table correspond to the metals directly weighed and suspended and corrected for purity, according to the results in Table 14. The results showed AE was generally better than AA for detecting these powders.

An important consideration for metal powder standards is the rate of sedimentation of the metal in oil. Even though a sample of metal powder may be completely detected by an instrument, a rapid settling rate would preclude using the powder as a standard. The results of sedimentation experiments with VMC metal powders are given in Table 16. This Table reports the cumulative percent decrease in concentration of the metal as measured at the corresponding settling time interval. The settling rates predicted from Stoke's Law are in poor agreement with the observed results. This may indicate that the particles in these samples were agglomerated.

The results of these experiments clearly indicate metal powder standards require additional consideration. The evaluation of domestically supplied fine metal powders has demonstrated the importance of using ultrafine metal powders (mean particle size less than 3000\AA) as standards. The only commercially available supply of ultrafine metal powders was located in Japan. However, even the ultrafine powders were not 100% analyzable by AA or emission spectroscopy.

TABLE 14
PURITY OF VMC METAL POWDERS

<u>Metal</u>	<u>Size</u>	1st Set Received		2nd
		<u>% Purity</u>	<u>Impurities</u>	Set Received
Ag	700Å	96.5	-	% Purity 100
Al	1000Å	86.7	3.5 (Cu)	91
Cu	300Å	94.6		-
Mg	2000Å	57.3	10.6 (Ag)	97
Ni	300Å	93.8		85
Ni	1000Å	97.8		-
Sn	1000Å	83.9		-

TABLE 15
ANALYZABILITY OF VMC METAL POWDERS

<u>Metal</u>	<u>VMC Size</u>	<u>Calc. (ppm)</u>	AA		AE
			<u>VMC1 (ppm)</u>	<u>VMC5 (ppm)</u>	<u>VMC1 (ppm)</u>
Ag	700Å	100	39.5	43.0	58
Al	1000Å	100	64.5	64.0	108
Cu	300Å	100	16.0	17.5	34
Mg	2000Å	100	18.5	16.5	62
Ni	300Å	100	95.0	95.5	97
Ni	1000Å	100	39.0		33
Sn	1000Å	100	57.3		63

TABLE 16
EFFECT OF VMC METAL POWDER SETTLING RATES

Time (minutes)	Cumulative Percent Decrease					
	Al (1000Å)	Ag (700Å)	Cu (300Å)	Ni (300Å)	Mg (2000Å)	Sn (1000Å)
- 100 ppm -						
0	----	----	----	----	----	----
9	----	----	----	----	----	9.5
14.5	6.4	6.4	13.9	2.1	----	----
16	----	----	----	----	----	19.0
24.8	7.3	10.6	16.7	5.2	9.5	----
35.3	2.7	12.8	16.7	5.2	12.7	----
77	----	----	----	----	----	31.7
80.3	14.5	23.4	27.8	14.6	7.9	----
208.3	23.6	35.1	36.1	25.0	25.4	----
1157.7	78.2	91.5	80.6	89.6	85.7	----
- 50 ppm -						
0	----	----	----	----	----	----
9	----	----	----	----	----	16.1
14.5	13.6	14.8	21.1	11.4	9.7	----
16	----	----	----	----	----	25.8
24.8	16.7	20.4	26.3	12.9	9.7	----
35.3	19.7	24.0	26.3	20.0	16.1	----
77	----	----	----	----	----	32.3
80.3	27.3	29.6	42.1	22.9	16.1	----
208.3	36.4	42.6	42.1	27.1	25.8	----
1157.7	80.3	87.0	78.9	85.1	83.9	----

SECTION III

EVALUATION OF STANDARDS

1. EVALUATION OF STANDARDS IN MIL-L-7808H, 245 BASE OIL, 170 PALE OIL AND PHILIPS CONDOR 105

a. Introduction

For oil calibration standards to be reliable, it is necessary to know their potential shelf life and stability. The stability of Conostan, JOAP-TSC, Cannon, metal caprates, metal thds, metal 2-ethylhexanoates, and NBS Standards were determined.

b. Experimental

(1) NBS10 Standards

The metal compounds listed in Table 17 were obtained from the National Bureau of Standards (NBS) and solubilized according to NBS procedures to give a metal concentration of 1000 ppm (NBS1-1000) in Mobil MIL-L-7808H ester oil. The resulting solutions were used to prepare a standard solution (NBS10-100) containing 100 ppm of each (ten) metals in a 4-oz. polyethylene bottle. Different quantities of the NBS10-100 solution were diluted with Mobil ester oil (MIL-L-7808H) to give the standard solutions NBS10-2, NBS10-5, NBS10-10, NBS10-20 and NBS10-50. The standard solutions were prepared on September 5, 1975 and the set labeled "duplicate" was prepared on September 26, 1975.

(2) Conostan 5000-PPM Standards

The 5000- ppm standards are prepared individually from metallo-organic alkyl aryl sulfonates and obtained from Conostan Division of the Continental Oil Company, Ponca City, Oklahoma. These standards were prepared by Conostan in 80 pale oil on the dates listed in Table 18.

TABLE 17
COMPOUNDS OBTAINED FROM NBS

<u>NBS Reference No.</u>	<u>Compound</u>	<u>% Metal</u>
1077a	Silver-2-Ethylhexanoate	42.1 \pm 0.05
1075a	Aluminum 2-Ethylhexanoate	8.07 \pm 0.02
1078b	Tris(1-phenyl-1,3-butanediono)-chromium (III)	9.6 \pm 0.1
1080a	Bis(1-phenyl-1,3-butanediono)-copper (II)	16.37 \pm 0.07
1079b1079b	Tris(1-phenyl-1,3-butanediono)-iron (III)	10.45 \pm 0.04
1061c	Magnesium Cyclohexanebutyrate	6.45 \pm 0.02
1065b	Nickel Cyclohexanebutyrate	13.89 \pm 0.02
1059b	Lead Cyclohexanebutyrate	36.65 \pm 0.06
1066a	Octaphenylcyclotetrasiloxane	14.14 \pm 0.07
1057b	Dibutyltin Bis(2-ethylhexanoate)	22.95 \pm 0.07

TABLE 18
DATES OF PREPARATION FOR 5000-PPM CONOSTAN STANDARDS

<u>Metal</u>	<u>Date Prepared</u>
Ag	November 11, 1974
Al	November 19, 1974
Cr	January 19, 1974
Cu	August 29, 1974
Fe	June 19, 1974
Mg	October 7, 1974
Mo	November 13, 1973
Ni	November 27, 1974
Pb	September 19, 1974
Si (not a sulfonate)	December 26, 1974
Sn	July 29, 1974
Ti	August 8, 1972

(3) C12 Standards

Equal weights of Ag, Al, Cr, Cu, Fe, Mg, Mo, Ni, Pb, Si, Sn and Ti 5000-ppm concentrates were diluted with MIL-L-7808H Mobil ester oil containing 0.6 percent amine sulfonate stabilizer to yield standard solutions containing 100 ppm of each metal (C12-100-0.6). Different quantities of the C12-100-0.6 solution were diluted with ester oil containing amine sulfonate stabilizer to yield standard solutions C12-2-0.6, C12-5-0.6, C12-10-0.6, C12-20-0.6 and C12-50-0.6. The standard solutions were prepared in this laboratory on September 5, 1975 and the set labeled "duplicate" was prepared on September 26, 1975.

(4) D12 Special Standards (Light Oil)

The D12 special standards were obtained from the Technical Support Center (TSC), Naval Air Rework Facility, Pensacola Naval Air Station, Pensacola, Florida. This set of standards was prepared from Conostan metallo-organic alkyl aryl sulfonate concentrates, 170 pale oil and 0.48 percent amine sulfonate stabilizer. The 100-ppm sample is similar but contains only 0.12 percent stabilizer. These standard solutions were obtained in concentrations of 3, 10, 30, 50 and 100 ppm and will be referred to as D12-3-0.48 (light oil), D12-10-0.48 (light oil), D12-30-0.48 (light oil), D12-50-0.48 (light oil) D12-100-0.12 (light oil) respectively. The D12 standards are prepared by TSC especially for the AA and A/E35U-1 spectrometers. These standard solutions were prepared by TSC on June 16, 1975 except for D12-50-0.48 (light oil) which was prepared on September 10, 1975.

(5) D13 Special Standards (Light Oil)

The D13 standard solutions were obtained from TSC and are prepared from Conostan metallo-organic alkyl aryl sulfonates, 170 pale oil, and 0.48 percent amine sulfonate stabilizer except for the 100 ppm standard which contains 0.12

percent stabilizer. In addition to the usual 12 metals sodium has been added. These samples will be referred to as D13-10-0.48 (light oil), D13-30-0.48 (light oil), D13-50-0.48 (light oil) and D13-100-0.12 (light oil) and were prepared by TSC on February 25, 1976.

(6) D12 Standards (Heavy Oil)

The D12 (heavy oil) samples were obtained from TSC and were prepared from Conostan metallo-organic alkyl aryl sulfonate concentrates, Conostan 245 base oil (a SAE 50, non-aromatic, hydrocarbon oil), and 0.48 percent amine sulfonate stabilizer. The 100 ppm sample is similar but contains only 0.12 percent stabilizer. These standard solutions will be referred to as D12-3-0.48, D12-10-0.48, D12-30-0.48, and D12-100-0.12 and were prepared by TSC on November 28, October 31, November 28, November 17 and November 18, 1975, respectively.

(7) D13 Standards (Heavy Oil)

The D13(D12+Na) standard solutions were obtained from TSC and are prepared from Conostan metallo-organic, alkyl aryl sulfonates, 245 base oil and 0.48 percent amine sulfonate stabilizer except for the D13-100 which contains 0.12 percent stabilizer. In addition to the usual 12 metals, sodium has been added. These samples will be referred to as D13-3-0.48 (heavy oil), D13-100.48 (heavy oil), D13-30-0.48 (heavy oil), D13-50-0.48 (heavy oil) and D13-100-0.12 (heavy oil) and were prepared by TSC on April 12, 1976.

(8) Cannon Standards (SP9)

The metal compounds used in Cannon standards are the same as those used by NBS. These standards contain specified concentrations of Ag, Al, Cr, Cu, Fe, Mg, Ni, Pb and Sn, supplied by Cannon Instrument Co., State College, PA., blended in Phillips Condor 105 hydrocarbon oil in concentrations of 1, 2, 3, 5, 10, and 20 ppm. These standards will be referred to as SP9-1, SP9-2, SP9-3, SP9-5, SP9-15, and SP9-20,

respectively. Standards containing only Al, Cr, Cu, Fe, Mg, Ni, Pb and Sn were obtained in concentrations of 50 and 100 ppm and will be referred to as SP8-50 and SP8-100, respectively. These standards were prepared by Cannon Instrument Co., on May 19, 1976.

(9) Metal Caprates (S8)

The metal caprates listed in Table 19 were synthesized and solubilized according to NBS Procedures to give a metal concentration of 800 ppm (S1-800) in MIL-L-7808H (Mobil) ester oil. The resulting solutions were used to prepare standard solutions containing 100, 50, 30, 20, 10, 5 and 2 ppm and will be referred to as S8-100, S8-50, S8-30, S8-20, S8-10, S8-5 and S8-2, respectively. The theoretical percent metal was used to calculate the concentrations of the metal caprates. These standards were prepared in this laboratory on June 29, 1976.

TABLE 19
METAL CAPRATES

Compound	% Metal theory	% Metal found by AFML/TUA	% Metal by AA in Mobil 7808 oil at 100 ppm
Silver Caprate	38.67	38.7	34.2%, 41.7%*
Copper Caprate	15.65	15.3	15.9
Aluminum Caprate	6.98	6.5	6.0
Chromium Caprate	13.75	14.2	12.3
Magnesium Caprate	6.63	5.2	6.8
Iron Caprate	9.80	9.6	10.0
Nickel Caprate	14.63	13.7	15.6
Lead Caprate	37.69	37.2	37.1

*Measured from 50 ppm rather than 100 ppm.

(10) Conostan Concentrates; C13 Standards

The Conostan concentrates are metallo-organo alkyl aryl sulfonates supplied by Conostan in the concentrations listed in Table 20. These concentrates were prepared by Conostan on the dates listed in Table 20. The Conostan concentrates are viscous liquids and are miscible with each other and oils.

Table 20 shows the concentrate weights needed in order to obtain a blend containing 0.25 g (2642 ppm) of each metal. The resulting blend will be referred to as C13-2642. The metal concentrations in the concentrates were determined by NBS and Conostan; however, the NBS values used by Pensacola were used in determining the weight of concentrate needed to obtain the desired metal concentration.

The Conostan concentrates contain Na and Fe as common contaminants, and these two elements were found in all the concentrates. To obtain the desired concentration of Fe and Na, the weight of Fe and Na concentrate needed must be corrected for the amount of Fe and Na in the other concentrates.

The correction calculations used in preparing Fe and Na concentrations are:

$$\begin{aligned} \text{g Na (Ag sample)} &= (\text{ppm Na}) \times (\text{g. conc} / 0.25 \text{g Ag}) \\ &= 120 \times 10^{-6} \times 4.931 = 592 \times 10^{-6} \text{g} \end{aligned}$$

$$\Sigma \text{ g Na (all samples)} \times 10^6 = 7083 \text{ g}$$

$$\% \text{ Na (Na sample)} \times 10^4 = 3.79 \times 10^4$$

$$\text{g Na Correction} = \frac{\Sigma \text{ g Na} \times 10^6}{\% \text{ Na} \times 10^4} = \frac{7083 \text{ g Na}}{3.79 \times 10^4} = 0.1869 \text{ g Na}$$

$$\text{corrected g conc.} / 0.25 \text{ g Na} = 6.596 - 0.187 = 6.409$$

$$\Sigma \text{ g Fe} \times 10^6 = 2744 \text{ g Fe}$$

$$\% \text{ Fe} \times 10^4 = 2.55 \times 10^4$$

TABLE 20
PREPARATION OF C13-2642 STANDARD

Metal	%M*	Date Prep. (Conostan)	g Conc./ 0.25gM	PPM Na	g Na x10 ⁶	PPM Fe	g Fe x10 ⁶	Corr. g Conc./ 0.25gM
Ag	5.07	Apr70	4.931	120	592	8	39	4.93
Al	2.29	Apr70	10.917	8	87	25	273	10.92
Cu	4.61	Jun70	5.423	170	922	37	201	5.42
Cr	1.89	Aug70	13.228	29	384	59	780	13.23
Mg	2.10	Apr70	11.905	248	2952	11	131	11.90
Fe	2.55	Aug70	9.804	59	578			9.70
Mo	2.10	Jun70	11.905	45	536	77	917	11.90
Ni	3.34	May70	7.485	110	823	19	142	7.49
Pb	9.92	Feb72	2.520	32	81	13	33	2.52
Si	13.11	May70	1.907	1	2	9	17	1.91
Sn	5.91	Apr70	4.230	23	97	19	80	4.23
Ti	6.13	Apr70	4.078	7	29	16	65	4.08
Na	3.79	May70	6.596			10	66	6.41
				Σ g Na = 7083		Σ g Fe = 2744		94.64

*NBS value

$$\text{g Fe correction} = \frac{\Sigma \text{ g Fe} \times 10^6}{\% \text{ Fe} \times 10^4} = \frac{2744 \text{ g Fe}}{2.55 \times 10^4} = 0.108 \text{ g Fe}$$

$$\text{Corrected g conc./0.25 g Fe} = 0.804 - 0.108 = 9.696 \text{ g}$$

Standards containing 100, 50, 30, 20, 15, 10, 5, 3, 2 and 1 ppm were prepared by diluting samples of C13-2642 with MIL-L-7808H (Mobil) oil. These samples will be referred to as C13-100, C13-50, C13-30, C13-20, C13-15, C13-10, C13-5, C13-3, C13-2 and C13-1, respectively.

(11) Metal 2-Ethylhexanoates (EA8)

Eight metal 2-ethylhexanoates were solubilized in MIL-L-7808H (Mobil) as single element concentrates and analyzed for metal content using Conostan Standards (Table 21). Based on the concentrations determined by AA, multielement standards were prepared which will be referred to as EA8-100, EA8-50, EA8-30 and EA8-10.

(12) Metal thd Standards (T12)

The metal 2,2,6,6-tetramethyl-3,5 heptanedionates (thds) were solubilized in ester oil in order to evaluate these compounds as possible primary standards. Since Ag and Si thds could not be prepared, NBS standards were used for these metals.

Each metal thd was solubilized in MIL-L-7808H ester oil to prepare concentrates as listed in Table 22. The concentrates were used to prepare T12-100, T12-50, T12-30, T12-10, and T12-3, which contain approximately 5% 2-ethylhexanoic acid as a stabilizer.

(13) Metal Acetates

The metal acetates are inexpensive and readily available organometallic compounds. Since other metal carboxylates such as metal 2-ethylhexanoates and metal caprates have been successfully solubilized, the metal acetates were

TABLE 21
DISSOLUTION OF METAL 2-ETHYLHEXANOATES

Compound	% Metal by AA	% Metal Theory	Conc of Concentrate (ppm)	% Solublizer
Cu	17.52	18.15	4823	27 EA**
Cr	12.32	10.80	5740	38 EA/MHD***
Ni	8.90	12.41	3220	18.4 EA
Mg	7.82	7.82	2712	EA
Fe	11.51	11.50	7949	EA
Al*	8.17	8.07	4439	NBS Procedure
Ti	7.72	7.70	5135	EA
Sn*	22.86	22.95	4652	NBS Procedure

* NBS Primary Standard

** EA = 2-ethylhexanoic acid

*** MHD = 6-methyl-2,4-heptanedione

TABLE 22
PREPARATION OF TI2 STANDARDS

Metal Comp	% Metal Calc.	% Metal Exp (AFML)	% Metal AA	% Solublizer	Conc (ppm)
Ag	42.60		40.81	NBS	4946
Al(thd) ₃	4.68	4.3	4.40	57.4 ² H(thd) ² , H(fod) ³ , xylene	5025
Cr(thd) ₃	8.64	8.7	8.41	19.7 EA ⁵	2514
Cu(thd) ₂	14.77	12.7	14.24	19.0 EA	5025
Fe(thd) ₃	9.22	8.4	8.79	16.5 EA	2514
Mg(thd) ₂	5.46	3.8	5.48	27.4 EA	2425
O ₂ Mo(thd) ₂	19.40	17.6	20.54	2.3 EA/MHD ⁴	5022
Ni(thd) ₂	13.81	13.6	13.36	21 EA	5028
Pb(thd) ₂	36.11	33.2	32.70	17.7 EA	5020
Si	14.13		12.50	NBS	2012
Cl ₂ Sn(thd) ₂	21.34	18.0	21.03	13.0 EA	5024
O Ti(thd) ₂	11.13		10.9	20 EA	4892

1. % Metal Calculated was used to prepare standards
2. H(thd) = 2,2,6,6-tetramethyl-3,5-heptanedione
3. H(fod) = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione
4. MHD = 6-methyl-2,4-heptanedione
5. EA = 2-ethylhexanoic acid

also investigated. Seven metal acetates, Pb, Cu, Mg, Ni, Ag, Al and Cr were dried over P_2O_5 under vacuum for 25 hr. The metal acetates were then solubilized in Mobil ester oil with a minimum quantity of 2-ethylhexanoic acid. Silver acetate was solubilized with 2-ethylhexylamine while Al and Cr acetates could not be dissolved. The Pb, Cu, Mg, Ni and Ag single element standards were then mutually diluted to five concentrations from 100 ppm to 3 ppm with ester oil. These solutions were referred to as A5 and were prepared in November, 1976. The expected concentration reported, Table 23, calculated is based on the stoichiometry of each metal acetate.

(14) H₂O Standards (MIL-H-5606 Hydraulic Fluid)

A mixture of B, Ba, Be, Cd, Mn, V, and Zn was prepared from the Conostan concentrates in the same manner as C13 (10 above). The seven-element standard was labeled C7 and contained 2423.6 ppm of each element. The C13 and C7 blends were mixed to make a C20 standards that contained 1264 ppm of each element. The C20-1264 was then diluted with MIL-H-5606 to prepare 100-, 50-, 30-, 10- and 3- ppm standards. The stability and shelf life of these standards were evaluated for one year.

c. Procedure

During the monthly test period, the standard solutions being evaluated for stability ("old") were compared to freshly prepared C12 standards ("new"). The "new" standards were prepared from 5000-ppm Conostan concentrates which were obtained from Conostan Division on dates listed in Table 18. The only difference between "new" and "old" is that the "new" standards were stored as 5000-ppm concentrates while the "old" standards were stored at concentrations between 2-100 ppm. Conostan has indicated that the 5000-ppm concentrates are stable for at least 18 months and has assured us that our samples are good. Therefore, we assume that any degradation of

the concentrates is negligible. Five grams of each standard, "old" and "new", were diluted with ten grams of methyl isobutyl ketone (MIBK). Likewise, NBS10, D12 (light oil) and D13 (light oil) were diluted with two parts MIBK by weight, while the D12 (heavy oil) was diluted with five parts MIBK by weight.

Starting with the test period of August 16, 1976, the C13 standards were used as the "new" primary standards instead of the C12 standards which were used during previous test periods.

The spectrometer was standardized at 0 ppm with MIL-L-7808H ester oil diluted with two parts MIBK (1:2) for the NBS10 and C12 standards. The 170 pale oil diluted with two parts MIBK (1:2) was used as 0 ppm for D12 (light oil) and D13 (light oil) and 245 base oil diluted with five parts MIBK (1:5) was used as 0 ppm for the D12 (heavy oil) standards.

d. Conditions of Analysis

(1) Analytical Instrumentation

The analyses were performed on a Perkin-Elmer 305B flame atomic absorption spectrophotometer.

(2) Signal Analysis

The output signal was fed into a Leeds and Northrup Speedomax W strip-chart recorder. For each standard solution, the signal was integrated for ten seconds.

(3) Sample Preparation

Each standard solution was shaken on a Burrell Wrist-Action shaker before being analyzed.

(4) Calibration Standards

C12 and C13 standards were prepared by this laboratory from Conostan metallo-organic alkyl aryl sulfonate concentrates, MIL-L-7808H (Mobil) ester oil, and amine (0.6 percent by weight) sulfonate stabilizer. These standards

are labeled "new".

(5) Calculations

The following formulas and symbols were used to complete and display the analytical data;

$$\text{Ratio (R)} = A_{\text{old}}/A_{\text{new}}$$

$$\text{Av R} = \frac{\sum R (\text{metal})}{\sum \text{Number of different concentrations studied for metal}}$$

e. Results and Discussion

Tables 23-33 summarize the averages R values obtained from the analyses of multielement standards in different types of oil. the standards were prepared at several concentrations in the range 0-100 ppm and were analyzed periodically in order to evaluate them for stability and shelf life. Normally, the standards were analyzed several times during the first 12-month interval and once at 18-, 24-, 30-, and 36-months from the date of preparation. For a particular element, the results are reported as the average of the ratios (R) of absorbances for the old calibration standard to the freshly prepared C13 standard. A \pm 5% deviation in R is considered to be within the experimental error. However, larger deviations are expected for Pb, Si and Sn because of the low sensitivity of the atomic absorption analysis of these elements at concentrations < 10 ppm.

The analytical results for metal acetates during the 18-month interval are listed in Table 23. The recent results favorably agree with the previous analytical data. This indicates that the acetates of the five metals are stable for at least 1.5 years.

Table 24 lists the average R values for eight metal 2-ethylhexanoates. Even though Mg, Fe and Ni continue to be 8, 12 and 27% high, respectively the analytical results show

that the metal 2-ethylhexanoates are stable for at least 9 months.

The metal thd's were analyzed five times during the first 12-months from the date of preparation. The analyses (Table 25) indicate that the metal thd's are stable for at least 1 year.

The Cannon standards were 2 years old when last analyzed (Table 26). The results were similar to those of previous evaluation periods.

The metal caprate results are listed in Table 27. During the 18-month interval, there were no significant changes in the averages of the analytical results.

The D12 and D13 standards in 170 pale oil were 1.5 and 2 years old respectively when last analyzed. The results (Tables 28 and 29) of the recent analyses were similar to the results previously obtained. D12 and D13 calibration standards in 245 base oil (Tables 30 and 31) were also evaluated for 2 years. There were no significant changes in the results during the 2 year period.

The summary of the average values for C12 and NBS10 standards in MIL-L-7808H ester oil over the three year evaluation period are listed in Tables 32 and 33 respectively. The results indicate that these standards are stable for at least three years.

The results of the shelf live evaluation for the H2O standards in MIL-H-5606 over the one year period are listed Tables 34-38. Silver and sodium showed a steady increase over the testing period for all the concentrations considered. In general, the results indicate that the H2O standards were stable for at least one year.

In conclusion, the calibration standards in hydrocarbon oils, synthetic ester oil and hydraulic fluid exhibited

stability at 0-100 ppm over their respective periods of evaluation. Presently the Air Force Oil Analysis Laboratories use the D20 standard in 1100 base heavy hydrocarbon oil to calibrate the A/E35U-3 spectrometers when analyzing for wear metals in used synthetic ester oils. The analyses of used ester oils for wear metals yield high results. Therefore, we believe that the C12 standards in Mobil 7808 will yield more accurate values for trace metals in used ester lubricating oils. These C12 standards should be used to calibrate the present Air Force spectrometers. Multielement calibration standards with less than 12 metals do not meet Air Force requirements. However, the 12 metal thd's standards synthesized in our laboratory and prepared in ester oil can be used to calibrate the Air Force spectrometers.

2. EVALUATION OF D20 and D13 STANDARDS IN 85 BASE OIL

a. Introduction

This study was undertaken at the request of the JOAP Technical Support Center (TSC), NAS, Pensacola, FL in order to evaluate the shelf life of standards in 85 Base Oil.

b. Experimental

(1) Background

The 245 Base Oil previously used by JOAP as the matrix in making the calibration standards is no longer being produced. Therefore, Conostan 85 base oil was considered by the TSC as the matrix for the calibration standards.

(2) Instrumentation

The analyses were carried out at Pensacola on an A/E35U-3 Spectrometer.

(3) Rationale

The investigation of Conostan standards in Base Oil is undertaken to provide an independent evaluation of shelf

life, stability, and compatibility of the D13 and D20 calibration standards in the new Conostan 85 Base Oil. This evaluation is necessary to determine the effects, if any, of this new oil matrix on the organometallic compounds in the D13 and D20 standards.

(4) Samples

The samples were prepared by the TSC in June 1977.

(5) Procedure

(a) D13-3, D13-10, D13-50, D13-100, D13-500, D13-900, D20-3, D20-10, D20-50, D20-100, D20-500, and D20-900 calibration standards are to be agitated prior to each analysis.

(b) A second set of standards as in (a) is not to be agitated prior to each analysis.

(c) A third set of standards as in (a) but not including the D13-900 or D20-900, is to undergo accelerated aging prior to each analysis, as follows: Cool to -30°C for one week bring to room temperature, heat to 50°C for 24 hrs, store at room temperature and analyze at the end of six months. This cycle is to be repeated again prior to 12-, 18-, and 24-month analysis intervals.

(d) The A/E35U-3 spectrometer will be standardized using freshly prepared 0- and 100-ppm standards in 85 Base Oil prior to each analysis interval.

(e) The 500- and 900-ppm standards will be diluted to 100 ppm with 85 Base Oil before each analysis interval.

(f) Data of ten burns per sample will be collected.

(g) The analyses will be performed at 1-, 6-, 12-, 18-, and 24-month intervals from date of preparation. Reports to TSC will be provided upon completion of each analysis interval. The final report will be the summary of all data

obtained from this study.

(6) Calculations

The mean, standard deviation, and relative standard deviation will be calculated for each sample as follows:

N = Number of analyses

X_i = Individual analysis

ΣX_i = Sum of the individual analyses

ΣX_i^2 = Sum of the squares of the individual analyses

$(\Sigma X_i)^2$ = Square of the sum of the individual analyses

\bar{X} = Mean, ppm

$$= \frac{\Sigma X_i}{N}$$

σ = Standard deviation, ppm

$$= \frac{N(\Sigma X_i^2) - (\Sigma X_i)^2}{N(N-1)}$$

σ = Relative standard deviation, percent

$$= \frac{100\sigma}{\bar{X}}$$

c. Results and Discussion

Tables 39-50 summarize the results obtained from the analyses of D13 and D20 standards 18 months after their preparation. In general, the standards agitated before analyses continue to be stable. For the D13 and D20 "not agitated" samples, boron, barium, magnesium, and zinc showed significant decreases in their concentration. Boron and zinc began to show

a decrease in the "not agitated" samples six months after standard preparation. At the 50- and 100-ppm concentration level, lead decreased by 50 and 12%, respectively. Magnesium dropped by 11 and 19% for the D20-100 and D13-100, respectively. Barium and zinc concentrations decreased to 86 and 90 ppm, respectively. Surprisingly, boron decreased more than 15% at 50-, 100-, and 500-ppm levels in the agitated samples.

TABLE 23
ANALYTICAL RESULTS FOR METAL ACETATES

<u>Prepared</u>	<u>Concentration (ppm)</u>				
	<u>Analyzed</u> <u>11/4/76</u>	<u>Analyzed</u> <u>2/9/77</u>	<u>Analyzed</u> <u>5/5/77</u>	<u>Analyzed</u> <u>9/2/77</u>	<u>Analyzed</u> <u>6/13/78</u>
Pb(OAc)₂					
100.0	94.0	88.5	97.0	89.1	92.0
52.2	48.4	46.6	48.0	47.8	47.0
30.0	27.4	27.2	30.6	27.4	27.3
9.9	9.2	8.9	10.3	9.1	9.2
3.2	3.0	3.0	3.0	3.0	3.1
Mg(OAc)₂					
100.2	97.5	97.5	100.0	99.5	98.0
52.3	51.1	50.9	51.5	51.0	50.5
30.1	26.9	29.6	29.7	29.9	29.4
9.9	9.9	9.9	9.9	9.8	9.2
3.2	3.3	3.3	3.2	3.2	3.0
Ag(OAc)					
123.7	79.0	103.7	106.0	110.6	103.0
50.4	38.8	43.9	44.5	43.0	42.0
30.0	24.6	26.1	27.6	27.7	24.9
10.2	7.8	8.8	9.2	7.5	9.6
3.0	2.3	2.9	2.9	2.6	2.6
Cu(OAc)₂					
96.8	84.7	85.3	88.0	92.1	87.0
50.5	44.8	45.6	44.5	44.6	44.5
29.1	25.9	25.9	26.4	26.4	26.7
9.6	8.7	8.7	8.7	8.7	8.4
3.1	2.8	2.9	2.8	2.8	2.8
Ni(OAc)₂					
97.1	86.3	90.6	89.0	95.2	94.0
50.7	44.6	45.0	49.5	47.9	50.0
29.2	24.8	26.8	26.1	29.0	30.0
9.6	9.6	9.8	9.8	10.0	9.9
3.1	3.3	3.3	3.2	3.1	3.3

TABLE 24
AVERAGE R VALUES FOR METAL 2-ETHYLHEXANOATE STANDARDS

Metal	9-2-77	1-6-78	4-19	6-13	1-16-79
Ag					
Al	0.94	0.95	0.89	0.89	0.87
Cr	1.08	1.04	1.04	0.99	1.04
Cu	1.00	1.01	1.02	0.97	1.01
Fe	1.11	1.13	1.12	1.12	1.13
Mg	1.10	1.07	1.07	1.08	1.07
Mo					
Ni	1.26	1.25	1.28	1.27	1.30
Pb					
Si					
Sn	0.93	0.96	1.01	1.06	1.01
Ti	1.18	1.04	0.98	1.03	1.03

TABLE 25
AVERAGE R VALUES FOR METAL THD (T12) STANDARDS

Metal	7-7-77	9-2	1-6-78	4-19	6-13	1-16-79
Ag	0.98	0.90	0.90	0.95	1.01	0.95
Al	0.95	0.92	0.92	0.93	0.91	0.94
Cr	0.96	0.95	0.95	0.94	0.93	0.94
Cu	0.98	0.98	1.00	0.99	0.98	1.00
Fe	0.94	0.92	0.99	0.95	0.98	0.98
Mg	0.86	0.91	0.90	0.90	0.89	0.91
Mo	0.88	0.92	0.88	0.81	0.85	0.91
Ni	0.98	1.01	0.90	0.99	1.00	1.03*
Pb	0.86	0.92	0.93	0.92	0.91	0.93
Si	0.94*	0.96	1.00	0.96	0.94	0.94
Sn	0.84*	0.86*	0.90	0.90	0.85	0.86
Ti	1.20	1.20	1.03	0.98	0.97	1.03

*3 ppm not included in average

TABLE 26
AVERAGE R VALUES FOR CANNON STANDARDS

Metal	11-4-76	8-16	2-9-77	5-5	6-6-78	6-13
Ag	1.08	1.06	1.14	1.11	1.06	1.10
Al	0.94	1.03	0.95	0.94	0.95	0.96
Cr	0.99	0.98	1.01	1.02	1.03	1.02
Cu	1.14	1.06	1.06	1.06	1.06	1.06
Fe	1.09	0.97	0.98	0.95	1.13	1.02
Mg	0.97	0.97	0.97	0.96	0.96	0.94
Mo						
Ni	0.95	0.98	0.95	1.15	0.97	0.96
Pb	0.97	0.93	0.96	0.94	0.95	0.97
Si						
Sn	1.10	0.81	0.99	1.14	0.99	0.90
Ti						

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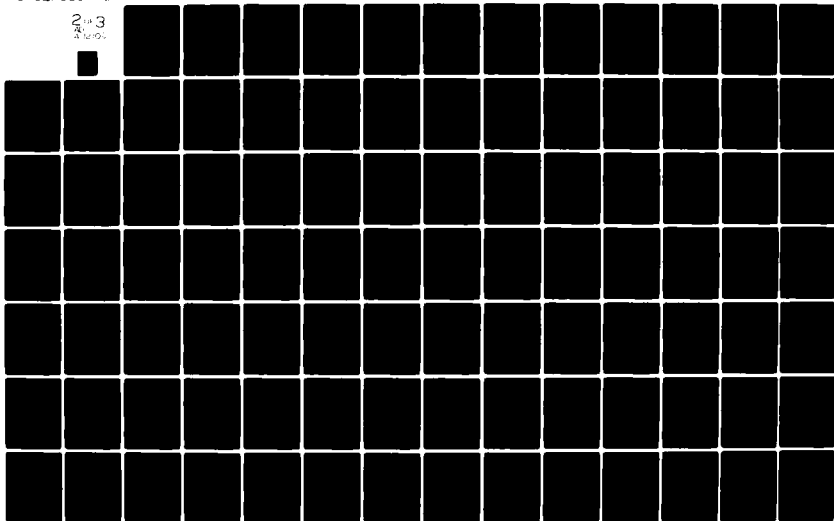
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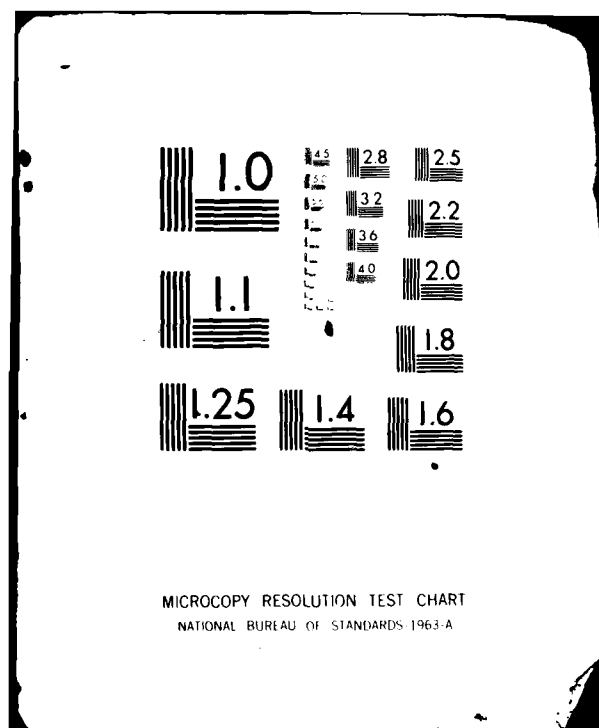


TABLE 27
AVERAGE R VALUES FOR CAPRATE STANDARDS

Metal	11-4-76	8-16	2-9-77	5-5	6-13-78
Ag	0.78	0.81	0.80	0.82	0.83
Al	0.90	0.90	0.90	0.89	0.91
Cr	0.85	0.84	0.86	0.86	0.88
Cu	1.07	1.06	1.06	1.07	1.08
Fe	0.92	1.02	0.96	0.98	1.01
Mg	1.03	1.01	1.03	1.03	1.03
Mo					
Ni	1.08	1.08	1.08	1.10	1.11
Pb	0.99	0.99	0.97	0.96	0.99
Si					
Sn					
Ti					

TABLE 28
AVERAGE R VALUES FOR D12 STANDARDS IN 170 PALE OIL

Metal	1-12-76	2-27	4-15	8-16	11-4	5-5-77
Ag	1.05	1.03	0.98	1.06	0.98	1.12
Al	0.95	0.96	1.02	1.04	1.00	0.98
Cr	0.97	1.01	1.00	1.01	1.01	1.04
Cu	0.97	0.98	1.01	1.07	1.03	1.03
Fe	1.00	1.04	0.97	1.06	1.12	1.06
Mg	0.94	0.97	1.00	1.02	1.00	1.04
Mo	0.86	0.89	0.91	0.86	0.84	0.85
Ni	0.98	1.01	0.94	1.03	1.01	1.06
Pb	0.90	1.00	1.02	1.04	1.05	1.00
Si	1.04	1.08	1.09	1.10	1.12	1.14
Sn	1.04	1.03	0.99	0.93	1.00	1.04
Ti	0.98	0.99	0.95	0.97	0.91	0.89

TABLE 29
AVERAGE R VALUES FOR D13 STANDARDS IN 170 PALE OIL

Metal	4-15-76	8-16	11-4	2-9-77	5-5	2-9-2	1-6-78
Ag	0.99	1.06	1.04	1.09	1.11	1.01	1.04
Al	1.04	1.03	1.00	1.03	1.00	1.03	1.00
Cr	1.02	1.04	1.02	1.04	1.06	1.01	1.02
Cu	1.01	1.06	1.02	1.03	1.03	1.03	1.02
Fe	0.99	1.06	1.08	1.05	1.05	1.06	1.05
Mg	1.00	1.02	0.98	0.99	1.04	0.99	1.00
Mo	0.96	0.97	0.93	0.93	0.96	1.01	0.97
Ni	0.96	1.02	1.03	1.02	1.06	1.03	1.04
Pb	0.94	1.06	1.05	1.04	1.05	0.98	1.03
Si	1.09	1.06	1.10	1.09	1.14	1.09	1.06
Sn	1.01	1.00	1.01	1.10	1.02	1.05	1.06
Ti	0.96	0.98	0.93	0.98	0.89	0.93	0.82

TABLE 30
AVERAGE R VALUES FOR D12 STANDARDS IN 245 BASE OIL

Metal	1-12-76	2-27	4-15	8-16	11-4	5-5-77	9-2
Ag	1.11	1.08	0.99	1.07	1.08	1.10	1.03
Al	0.99	0.99	1.02	1.01	0.97	0.97	1.11
Cr	0.98	1.03	1.01	1.00	0.99	0.97	0.96
Cu	0.96	0.99	1.03	1.06	1.07	1.12	1.01
Fe	1.00	0.99	1.00	1.09	1.05	1.00	1.00
Mg	0.93	0.97	1.00	0.99	0.94	0.97	0.95
Mo	0.94	1.00	0.98	0.92	0.91	0.97	0.94
Ni	0.97	1.02	0.92	1.09	1.02	0.99	1.00
Pb	1.01	0.96	1.00	1.02	1.04	1.05	1.20
Si	1.06	1.13	1.17	1.13	1.07	1.16	0.97
Sn	0.97	1.13	0.98	0.92	0.97	0.98	0.97
Ti	1.09	1.09	1.00	1.04	1.06	1.18	1.06

TABLE 31
AVERAGE R VALUES FOR D13 STANDARDS IN 245 BASE OIL

Metal	8-16-76	11-4	2-9-77	5-5	9-2	1-6-78	4-19
Ag	1.05	1.05	1.08	1.09	1.00	1.06	1.05
Al	0.99	0.95	0.97	0.99	1.13	0.98	0.97
Cr	1.02	1.01	0.99	1.00	0.99	1.03	1.01
Cu	1.06	1.05	1.00	1.12	1.00	1.05	1.05
Fe	1.08	1.03	1.01	1.04	0.99	1.09	1.04
Mg	0.99	0.94	0.97	0.97	0.96	0.94	0.98
Mo	0.92	0.90	0.97	0.94	0.93	0.86	0.83
Ni	1.08	1.02	0.97	1.00	1.00	1.05	1.02
Pb	1.00	1.01	1.02	1.02	1.20	0.99	1.00
Si	1.11	1.03	1.07	1.11	1.04	0.96	1.02
Sn	0.95	1.00	0.97	0.96	1.00	1.12	1.10
Ti	0.96	1.02	0.99	1.09	1.00	0.99	1.01

TABLE 32
AVERAGE R VALUE FOR C12 STANDARDS

Metal	9-26-75	10-24	12-3	1-12-76	2-27	4-15	8-16	11-4	5-5-77	9-2	9-13-78
Ag	1.00	1.05	0.96	1.04	1.05	0.98	1.00	0.98	1.01	0.92	0.95
Al	0.99	1.01	0.97	1.00	0.98	1.02	1.00	1.01	1.00	1.02	1.00
Cr	1.00	1.00	0.98	0.95	0.98	1.00	0.97	0.97	0.98	0.96	0.98
Cu	1.00	1.00	0.99	0.98	0.98	1.01	1.01	1.03	1.01	1.02	1.02
Fe	1.00	1.01	0.99	1.01	0.94	1.00	1.04	0.95	1.04	1.00	1.03
Mg	1.02	1.01	1.00	0.98	0.98	1.00	0.93	0.83	0.86	0.83	0.94
Mo	0.99	1.00	0.99	0.95	0.98	0.95	0.94	0.94	0.96	1.01	1.03
Ni	1.00	1.00	0.96	0.98	0.99	0.96	0.98	1.01	1.02	1.03	0.98
Pb	1.07	0.96	1.01	0.87	1.13	1.01	0.96	0.98	0.99	1.04	0.98
Si	1.00	1.00	0.95	0.96	0.94	1.10	0.90	0.92	0.91	0.95	0.91
Sn	0.99	1.00	0.97	0.94	0.98	1.02	0.95	0.99	1.04	0.95	0.97
Ti	1.00	1.01	0.97	0.97	0.99	1.00	0.98	0.98	0.97	1.00	0.96

TABLE 33
AVERAGE R VALUES FOR NBS10 STANDARDS

Metal	9-26-75	10-24	12-3	1-12-76	2-27	4-15	8-16	11-4	5-5-77	9-2	9-13-78
Ag	0.96	1.02	0.92	1.00	0.94	0.93	0.99	0.94	1.03	0.93	0.93
Al	1.00	0.97	0.93	0.97	0.96	0.98	1.03	0.98	0.98	1.00	1.01
Cr	0.98	0.96	0.96	0.94	0.95	0.98	0.93	0.91	0.93	0.97	0.94
Cu	0.99	1.01	0.98	1.00	1.00	1.03	1.00	1.01	1.00	1.01	1.03
Fe	0.96	0.98	0.92	0.96	0.96	0.97	0.97	0.93	0.98	0.98	1.03
Mg	0.97	0.98	0.96	0.94	0.96	0.99	0.99	0.98	1.01	1.02	0.99
Mo											
Ni	0.97	0.95	0.92	0.95	0.96	0.92	1.01	0.97	0.99	1.01	1.02
Pb	1.00	0.92	0.98	0.84	1.07	0.94	0.95	0.96	0.95	0.96	0.97
Si	1.01	0.99	0.94	0.94	0.96	1.05	0.85	0.93	0.90	0.88	0.92
Sn	1.05	0.94	0.98	0.92	0.98	0.89	0.90	0.94	1.00	0.98	0.98
Ti											

TABLE 34
EVALUATION OF H2O-100 STANDARD IN HYDRAULIC FLUID

<u>Element</u>	<u>2/24/80</u> <u>2 days</u>	<u>3/25/80</u> <u>one month</u>	<u>9/13/80</u> <u>7 month</u>	<u>3/19/81</u> <u>1 year</u>
Ag	100	97.8	101.9	102.7
Al	100	98.2	102.6	104.9
Ba	100	97.8	102.6	105.8
Cd	100	99.2	100.5	104.2
Cr	100	98.7	102.5	105.4
Cu	100	98.1	102.3	100.9
Fe	100	98.7	102.2	103.8
Mg	100	98.7	102.2	104.6
Mn	100	98.7	102.1	105.2
Mo	100	97.7	103.0	103.8
Na	100	100.0	102.5	102.3
Ni	100	98.7	103.3	104.7
Pb	100	96.8	103.0	103.6
Si	100	97.2	103.1	104.6
Sn	100	97.2	102.0	104.7
Ti	100	97.8	103.6	105.8
V	100	97.5	102.3	105.5
Zn	100	98.2	102.0	103.9

TABLE 35
EVALUATION OF H2O STANDARD IN HYDRAULIC FLUID

<u>Element</u>	<u>2/24/80</u> <u>2 days</u>	<u>3/25/80</u> <u>one month</u>	<u>9/12/80</u> <u>7 month</u>	<u>3/19/81</u> <u>1 year</u>
Ag	50.6	53.1	54.0	56.5
Al	46.9	46.2	47.7	48.2
Ba	43.4	43.8	43.0	43.7
Cd	48.0	48.5	48.8	49.9
Cr	46.8	47.5	46.5	46.9
Cu	49.4	50.4	52.8	55.9
Fe	47.0	47.8	47.5	48.3
Mg	46.0	46.8	47.1	48.8
Mn	47.3	46.7	48.6	48.8
Mo	47.0	47.7	50.2	49.4
Na	57.3	61.2	63.6	68.5
Ni	45.1	45.8	48.0	47.8
Pb	46.2	47.0	49.2	49.6
Si	49.2	48.1	49.7	51.1
Sn	46.8	47.0	47.3	47.5
Ti	43.1	45.1	44.9	44.9
V	46.3	46.4	47.0	48.6
Zn	45.5	48.4	49.2	50.1

TABLE 36
EVALUATION OF H2O-30 STANDARD IN HYDRAULIC FLUID

<u>Element</u>	<u>2/24/80 2 days</u>	<u>3/25/80 one month</u>	<u>9/12/80 7 month</u>	<u>3/19/81 1 year</u>
Ag	31.9	34.2	34.5	37.4
Al	27.9	27.4	28.2	28.9
Ba	25.0	26.0	25.4	26.1
Cd	29.9	30.5	30.9	31.2
Cr	28.6	29.5	27.6	28.1
Cu	30.7	31.3	32.9	35.3
Fe	28.9	29.6	29.4	29.8
Mg	28.0	28.8	28.5	31.1
Mn	29.5	28.4	30.2	30.4
Mo	29.0	29.0	30.3	30.1
Na	36.6	40.1	42.0	47.8
Ni	27.5	28.2	28.0	29.3
Pb	28.0	28.7	29.5	30.3
Si	30.7	29.9	30.8	32.4
Sn	28.0	28.8	27.7	29.4
Ti	25.4	27.1	26.2	26.8
V	28.7	27.7	27.0	30.5
Zn	30.3	30.6	31.1	31.5

TABLE 37
EVALUATION OF H2O-10 STANDARD IN HYDRAULIC FLUID

Element	2/24/80 2 days	3/25/80 one month	9/12/80 7 month	3/19/81 1 year
Ag	10.8	12.2	11.5	13.1
Al	9.0	8.9	8.6	9.2
Ba	7.7	8.4	7.1	8.0
Cd	10.2	10.5	10.2	10.9
Cr	9.8	9.7	8.3	9.1
Cu	10.2	10.6	10.8	12.2
Fe	9.8	10.3	9.6	9.9
Mg	9.2	9.7	9.3	11.6
Mn	10.7	9.5	10.7	10.9
Mo	9.9	9.8	9.1	9.7
Na	12.7	14.5	14.1	17.4
Ni	8.8	9.3	8.8	9.8
Pb	9.5	9.6	8.4	9.5
Si	10.1	10.3	10.2	10.7
Sn	9.2	9.4	8.5	9.0
Ti	7.8	8.8	7.8	8.6
V	9.0	9.4	7.8	10.4
Zn	10.5	10.5	10.5	10.7

TABLE 38
EVALUATION OF H2O-3 STANDARD IN HYDRAULIC FLUID

<u>Element</u>	<u>2/24/80</u> <u>2 days</u>	<u>3/25/80</u> <u>one month</u>	<u>9/12/80</u> <u>7 month</u>	<u>3/19/81</u> <u>1 year</u>
Ag	3.2	3.8	3.2	4.0
Al	2.8	2.6	2.4	2.8
Ba	1.9	2.4	1.6	2.5
Cd	3.1	3.2	2.9	3.2
Cr	3.0	3.1	2.3	2.5
Cu	3.0	3.1	3.1	3.6
Fe	3.0	3.2	2.7	3.0
Mg	2.9	3.1	2.7	3.9
Mn	3.5	2.8	3.2	3.3
Mo	3.0	3.0	2.3	3.0
Na	3.9	4.2	4.0	5.6
Ni	2.6	3.0	2.4	2.6
Pb	2.8	3.1	2.6	3.2
Si	3.1	3.1	2.8	3.4
Sn	2.7	2.6	2.4	2.7
Ti	2.2	2.5	2.2	2.6
V	2.9	3.0	3.4	3.9
Zn	3.2	3.3	3.0	3.4

TABLE 39

SUMMARY OF DATA

FIVE ANALYSES EACH OF D13-3, D13-10, AND D13-50 CALIBRATION STANDARDS IN
CONOSTAN #85 BASE OIL, NOT AGITATED BEFORE ANALYSIS
A/E35U-3 SPECTROMETER STANDARDIZED WITH D13-0 AND D13-100 (#85 BASE OIL) STANDARDS

19 January 1979

Spectrometric Analysis

	Fe	Ag	Al	Cr	Cu	Mg	Na	Mn	Pb	Si	Sn	Ti	Zn
D13-3													
\bar{x} , ppm	2.77	2.91	2.48	2.83	2.43	2.86	1.75	2.49	2.45	2.70	3.12	2.91	2.75
σ , ppm	0.26	0.34	0.36	0.4	0.30	0.22	0.46	0.48	0.51	0.38	0.61	0.24	0.30
σ , percent	9.4	11.5	14.3	14.3	12.3	7.7	26.0	19.1	20.7	14.0	19.5	8.25	10.8
D13-10													
\bar{x} , ppm	9.59	10.27	9.73	9.90	8.97	9.79	9.90	9.70	9.09	9.53	9.93	9.85	9.17
σ , ppm	0.07	0.33	0.37	0.38	0.34	0.15	0.40	0.75	0.43	0.26	0.49	0.23	0.30
σ , percent	0.7	3.2	3.8	3.8	3.8	1.5	4	7.7	4.7	2.7	5.0	2.3	3.29
D13-50													
\bar{x} , ppm	47.71	46.90	48.21	48.32	47.39	46.45	44.90	46.35	7.85	49.28	46.96	47.38	45.20
σ , ppm	0.78	0.89	1.74	0.80	0.49	0.84	5.04	0.57	1.16	1.22	0.87	0.66	0.82
σ , percent	1.6	1.9	3.6	1.7	1.0	1.8	11.2	1.2	14.8	2.5	1.8	1.4	1.8

TABLE 40

SUMMARY OF DATA

FIVE ANALYSES EACH OF D13-100, D13-500, AND D13-900 CALIBRATION STANDARDS IN
CONOSTAN #85 BASE OIL, NOT AGITATED BEFORE ANALYSIS

A/E35U-3 SPECTROMETER STANDARDIZED WITH D13-0 AND D13-100 (#85 BASE OIL) STANDARDS

19 January 1979

Spectrometric Analysis

	Fe	Ag	Al	Cr	Cu	Mg	Na	Ni	Pb	Si	Sn	Ti	Mo
D13-100													
\bar{x} , ppm	92.8	94.3	91.6	93.3	93.9	81.4	85.3	92.8	88.7	95.3	96.5	94.0	92.4
σ , ppm	2.15	1.38	1.07	1.09	0.45	2.10	4.14	2.03	0.51	2.38	1.02	2.53	3.61
σ' , percent	2.3	1.5	1.2	1.2	0.5	2.6	4.9	2.2	0.6	2.5	1.1	2.7	3.9
D13-500													
\bar{x} , ppm	97.7	99.9	96.7	96.0	98.0	96.4	91.0	96.7	96.7	97.5	101.6	96.6	97.6
σ , ppm	1.49	1.81	1.15	0	0.99	1.86	4.71	2.36	1.47	2.73	1.15	2	2.46
σ' , percent	1.5	1.8	1.2	0	1.0	1.9	5.2	2.4	1.5	2.8	1.1	3.1	2.5
D13-900													
\bar{x} , ppm	100.4	100.6	100.3	99.6	99.4	98.16	92.9	98.6	98.2	102.3	105.6	99.7	100.4
σ , ppm	1.64	2.17	3.07	2.49	1.80	1.47	6.31	2.25	1.81	3.47	2.46	2.39	3.26
σ' , percent	1.6	2.2	3.1	2.5	1.8	1.5	6.8	2.3	1.8	3.4	2.3	2.4	3.2

TABLE 41
SUMMARY OF DATA
FIVE ANALYSES EACH OF D13-3, D13-10, AND D13-50 CALIBRATION STANDARDS IN
CONOSTAN #85 BASE OIL, AGITATED BEFORE ANALYSIS
A/E35U-3 SPECTROMETER STANDARDIZED WITH D13-0 AND D13-100 (#85 BASE OIL) STANDARDS
19 January 1979

Spectrometric Analysis														
	Fe	Ag	Al	Cr	Cu	Mg	Na	Ni	Pb	Si	Sn	Ti	Mo	
D13-3														
\bar{X} , ppm	2.76	2.74	2.31	2.23	2.35	2.92	2.10	2.06	2.36	2.88	2.85	2.83	2.86	
σ , ppm	0.35	0.24	0.60	0.26	0.29	0.15	0.42	0.67	0.29	0.28	0.47	0.29	0.21	
σ' , percent	12.8	8.7	25.7	11.9	12.3	5.10	20.0	32.6	11.2	9.7	16.4	10.3	7.4	
D13-10														
\bar{X} , ppm	9.51	10	8.93	9.41	8.57	9.65	9.50	9.1	8.91	9.81	10.2	10	9.55	
σ , ppm	0.37	0.50	0.68	0.46	0.46	0.38	0.41	0.81	0.35	0.44	0.90	0.43	0.29	
σ' , percent	3.9	5.0	7.6	4.8	5.4	4.0	4.3	8.9	3.9	4.5	8.8	4.3	3.0	
D13-50														
\bar{X} , ppm	46.52	45.30	45.71	47.14	47.87	46.73	44.43	47.04	46.90	46.29	45.61	46.60	42.99	
σ , ppm	0.36	0.60	1.04	0.71	0.70	0.39	2.82	1.04	0.83	0.86	0.78	0.32	1.49	
σ' , percent	0.8	1.3	2.3	1.5	1.5	0.8	6.3	2.2	1.8	1.8	1.7	0.69	3.48	

TABLE 42

SUMMARY OF DATA

FIVE ANALYSES EACH OF D13-100, D13-500, AND D13-900 CALIBRATION STANDARDS IN CONOSTAN #85 BASE OIL, AGITATED BEFORE ANALYSIS

A/E35U-3 SPECTROMETER STANDARDIZED WITH D13-0 AND D13-100 (#85 BASE OIL) STANDARDS

19 January 1979

Spectrometric Analysis

	Fe	Ag	Al	Cr	Cu	Mg	Na	Mn	Pb	Si	Sn	Ti	Mo
D13-100													
\bar{X} , ppm	93.5	95.0	93.9	94.3	95.1	94.3	85.8	93.9	95.8	94.5	98.3	92.4	90.7
σ , ppm	1.49	2.65	2.82	1.90	3.01	1.76	1.49	2.63	1.86	1.21	1.93	1.65	2.74
σ , percent	1.6	2.8	3.0	2.0	3.2	1.9	1.7	2.8	1.94	1.3	2.0	1.8	3.0
D13-500													
\bar{X} , ppm	98.2	100.8	98.2	97.6	98.6	96.6	91.4	97.3	95.8	99.1	103.0	97.9	99.6
σ , ppm	0.44	1.91	1.07	1.13	0.88	0.69	5.14	1.75	1.13	2.29	1.37	1.20	2.95
σ , percent	0.4	1.9	1.1	1.2	0.9	0.7	5.6	1.8	1.2	2.3	1.3	1.2	3.0
D13-900													
\bar{X} , ppm	98.4	100.8	98.2	99.4	99.0	96.0	96.6	98.0	96.2	101.1	104.5	98.6	99.7
σ , ppm	1.49	2.01	3.01	1.50	2.10	1.47	7.86	2.08	1.55	3.83	1.63	1.12	4.60
σ , percent	1.5	2.0	3.1	1.5	2.1	1.5	7.9	2.1	1.6	3.8	1.6	1.1	4.6

TABLE 43

SUMMARY OF DATA

FIVE ANALYSES EACH OF D13-3, D13-10, AND D13-50 CALIBRATION STANDARDS IN CONOSTAN #85 BASE OIL, COOLED, HEATED, AND AGITATED BEFORE ANALYSIS
A/E35U-3 SPECTROMETER STANDARDIZED WITH D13-0 AND D13-100 (#85 BASE OIL) STANDARDS

19 January 1979

Spectrometric Analysis

	Fe	Ag	Al	Cr	Cu	Mg	Na	NI	Pb	Si	Sn	Ti	Mo
D13-3													
\bar{X} , ppm	2.77	3	3.06	3.03	2.58	2.92	3.97	2.71	2.71	2.61	2.32	2.91	2.65
σ , ppm	0.29	0.35	0.52	0.36	0.33	0.24	0.49	0.73	0.44	0.28	0.26	0.37	0.40
σ' , percent	10.6	11.8	17.0	12.0	12.7	8.2	12.4	26.8	16.1	10.7	11.2	12.8	15.2
D13-10													
\bar{X} , ppm	9.01	9.82	9.64	9.41	8.57	9.17	9.60	8.90	9.00	9.25	8.45	9.10	8.78
σ , ppm	0.46	0.54	0.44	0.49	0.48	0.35	0.19	0.65	0.59	0.47	0.93	0.38	0.49
σ' , percent	5.1	5.5	4.5	5.2	5.6	3.9	1.96	7.30	6.6	5.1	11.0	4.18	5.5
D13-50													
\bar{X} , ppm	48.46	46.80	46.73	47.11	46.60	49.08	45.77	47.37	50.37	48.73	45.36	48.58	48.46
σ , ppm	1.97	1.92	2.93	1.13	0.84	2.15	2.29	1.47	2.54	2.03	2.05	1.36	1.59
σ' , percent	4.1	4.1	6.3	2.4	1.8	4.4	5.0	3.10	5.0	4.2	4.5	2.8	3.3

TABLE 44

SUMMARY OF DATA

FIVE ANALYSES EACH OF D13-100 AND D13-500 CALIBRATION STANDARDS IN CONOSTAN
#85 BASE OIL, COOLED, HEATED, AND AGITATED BEFORE ANALYSIS
A/E35U-3 SPECTROMETER STANDARDIZED WITH D13-0 AND D13-100 (#85 BASE OIL) STANDARDS

19 January 1979

Spectrometric Analysis

	Fe	Ag	Al	Cr	Cu	Mg	Na	Kl	Pb	Si	Sn	Ti	Mo
D13-100													
\bar{X} , ppm	99.8	100.2	96.7	95.3	99.2	99.4	94.5	99.3	97.4	93.0	94.6	97.3	96.8
σ , ppm	2.11	4.12	1.92	0.86	2.15	2.65	4.24	3.25	1.52	1.62	1.97	2.49	3.79
σ , percent	2.2	4.1	2.0	0.90	2.2	2.7	4.5	3.3	1.6	1.8	2.1	2.6	3.9
D13-500													
\bar{X} , ppm	99.8	107.0	99.1	98.7	103.0	102.9	104.6	101.7	100.2	95.2	99.8	101.1	97.7
σ , ppm	1.59	3.9	1.96	1.43	2.62	2.86	6.67	2.85	1.20	3.30	1.10	1.86	4.84
σ , percent	1.6	3.7	2.0	1.4	2.5	2.8	6.4	2.8	1.2	3.5	1.1	1.8	5.0

TABLE 45

SUMMARY OF DATA

FIVE ANALYSES EACH OF D20-3, D20-10, AND D20-50 CALIBRATION STANDARDS IN
CONOSTAN #85 BASE OIL, NOT AGITATED BEFORE ANALYSIS
A/E35U-3 SPECTROMETER STANDARDIZED WITH D20-0 AND D20-100 (#85 BASE OIL) STANDARDS

19 January 1979

Spectrometric Analysis

	Fe	Ag	Al	Be	Cr	Cu	Hg	Na	Ni	Pb	Si	Sn	Ti	B	Ba	Cd	Mn	Mo	V	Zn
D20-3																				
\bar{x} , ppm	3.11	3.30	3.69	2.28	2.8	2.84	3.50	2.29	2.25	2.50	2.79	3.14	3.25	3.83	2.61	2.89	2.79	3.83	2.93	3.33
σ , ppm	0.24	0.16	0.44	0.09	0.22	0.21	0.10	0.43	0.57	0.47	0.20	0.70	0.20	0.21	0.15	0.28	0.18	0.27	0.66	0.15
σ %, percent	7.5	4.7	11.9	3.9	7.9	7.3	2.9	18.7	25.2	18.9	7.2	22.3	6.2	5.61	5.7	9.7	6.3	7.0	29.3	4.5
D20-10																				
\bar{x} , ppm	10.36	11.07	10.24	6.06	9.8	10.32	12.52	9.88	9.2	8.40	9.90	10.72	11.4	8.69	10.16	10.35	10.80	11.23	9.56	10.98
σ , ppm	0.38	0.34	0.33	0.29	0.33	0.35	0.17	0.22	0.48	0.18	0.61	0.54	0.40	0.37	0.42	0.56	0.22	0.73	0.89	0.89
σ %, percent	3.64	3.1	3.2	4.8	3.4	3.4	1.40	2.2	5.2	2.1	6.2	5.0	3.5	4.3	4.1	5.4	2.1	6.5	9.3	8.1
D20-50																				
\bar{x} , ppm	48.43	48.74	47.63	48.93	48.60	48.27	47.78	49.88	45.53	41.38	47.60	47.24	46.80	12.8	40.19	48.36	48.15	51.39	46.24	50.64
σ , ppm	1.37	1.0	1.08	1.63	0.69	0.89	1.34	1.84	0.99	1.11	0.98	1.02	1.40	0.44	0.92	1.52	1.28	1.91	1.25	3.33
σ %, percent	2.8	2.0	2.3	3.3	1.4	1.8	2.8	3.7	2.2	2.68	2.1	2.2	3.0	3.4	2.3	3.15	2.6	3.7	2.7	6.6

TABLE 46

SUMMARY OF DATA

FIVE ANALYSES EACH OF D20-100, D20-500, AND D20-900 CALIBRATION STANDARDS
IN CONOSTAN #85 BASE OIL, NOT AGITATED BEFORE ANALYSIS

A/E35U-3 SPECTROMETER STANDARDIZED WITH D20-0 AND D20-100 (#85 BASE OIL) STANDARDS

19 January 1979

Spectrometric Analysis

	Fe	Ag	Al	Be	Cr	Cu	Mg	Na	Ni	Pb	Si	Sn	Ti	B	Ba	Cd	Mn	Mo	V	Zn
D20-100																				
\bar{x} , ppm	93.7	93.0	94.9	95.5	93.4	93.9	89.1	92.4	93.0	90.6	95.2	96.3	94.7	22.6	86.5	95.1	95.0	97.6	92.7	90.6
σ , ppm	2.46	3.46	1.56	1.53	1.14	2.62	3.21	3.28	2.50	2.06	0.68	2.10	3.64	0.78	2.23	3.27	2.19	4.57	2.85	9.16
σ , percent	2.6	3.7	1.64	1.7	1.2	2.8	3.6	3.6	2.7	2.3	0.7	2.2	3.8	3.5	2.6	3.4	2.3	4.7	3.1	10.1
D20-500																				
\bar{x} , ppm	99.8	97.4	98.9	100.0	99.4	98.9	100.1	99.2	97.9	97.2	100.7	99.7	99.9	68.4	97.5	102.6	100.1	101.1	97.9	102.8
σ , ppm	2.83	3.10	1.89	3.18	1.64	2.53	2.25	3.16	2.89	2.16	4.06	2.43	3.55	1.70	3.26	2.22	2.46	4.74	2.63	7.40
σ , percent	2.8	3.2	1.9	3.2	1.7	2.6	2.3	3.2	3.0	2.2	4.03	2.4	3.6	2.5	3.3	2.2	2.5	4.7	2.7	7.2
D20-900																				
\bar{x} , ppm	97.2	96.6	98.7	97.2	98.6	98.5	98.2	99.9	98.5	95.8	98.0	97.9	96.3	70.7	95.8	99.1	98.2	95.1	97.7	94.0
σ , ppm	3.19	3.55	2.41	3.96	1.67	1.88	2.93	1.01	1.27	1.84	4.06	2.27	3.18	1.56	3.66	3.85	3.32	5.63	1.64	6.40
σ , percent	3.3	3.7	2.4	4.1	1.7	1.9	3.0	1.0	1.3	1.9	4.1	2.3	3.3	2.21	3.8	3.9	3.4	5.9	1.7	6.8

SUMMARY OF DATA

19 January 1979

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TABLE 48

SUMMARY OF DATA

FIVE ANALYSES EACH OF D20-100, D20-500, AND D20-900 CALIBRATION STANDARDS
IN CONOSTAN #85 BASE OIL, AGITATED BEFORE ANALYSIS
A/E35U-3 SPECTROMETER STANDARDIZED WITH D20-0 AND D20-100 (#85 BASE OIL) STANDARDS

19 January 1979

Spectrometric Analysis

	Fe	Ag	Al	Be	Cr	Cu	Hg	Na	Ni	Pb	Si	Sn	Ti	S	Ba	Cd	Mn	Mo	V	Zn
D20-100																				
X, ppm	95.9	97.2	93.2	95.4	94.7	94.4	96.7	97.6	94.4	95.8	96.0	93.5	96.1	86.5	97.3	97.3	95.7	102.0	94.0	94.0
s, ppm	2.17	1.82	0.72	2.69	0.89	1.26	1.43	3.66	1.37	0.99	1.88	0.96	1.52	3.11	1.14	2.80	1.45	4.16	0.44	8.88
s ² , percent	2.3	1.9	0.8	2.8	0.9	1.3	1.5	3.8	1.45	1.0	2.0	1.0	1.6	3.6	1.2	2.9	1.51	4.1	0.47	9.5
D20-500																				
X, ppm	100.2	97.6	98.7	99.8	99.8	99.1	99.7	99.9	98.9	98.7	100.7	99.8	100.3	83.6	98.6	100.6	100.5	100.4	98.3	97.2
s, ppm	3.11	4.59	2.80	2.99	1.82	2.16	2.77	3.77	2.54	2.29	2.68	2.91	3.78	2.37	3.35	4.21	2.48	4.64	2.24	11.67
s ² , percent	3.1	4.7	2.8	3.0	1.8	2.2	2.8	3.8	2.6	2.3	2.7	2.9	3.8	2.8	3.4	4.2	2.5	4.6	2.3	12.0
D20-900																				
X, ppm	98.8	99.9	99.0	99.2	99.6	99.8	98.1	100.7	97.9	99.4	100.3	99.3	98.6	97.7	98.4	100.4	99.3	98.3	98.5	101.3
s, ppm	1.37	3.72	2.14	1.34	1.14	1.07	2.25	1.11	1.30	2.32	2.14	2.60	1.66	2.30	2.83	2.6	1.27	2.83	1.49	12.30
s ² , percent	1.4	3.7	2.2	1.3	1.1	1.1	2.3	1.1	1.3	2.3	2.1	2.6	1.7	2.3	2.9	2.6	1.3	2.9	1.5	11.8

TABLE 49

SUMMARY OF DATA

FIVE ANALYSES EACH OF D20-3, D20-10, AND D20-50 CALIBRATION STANDARDS IN CONOSTAN #85 BASE OIL, COOLED, HEATED, AND AGITATED BEFORE ANALYSIS
A/E35U-3 SPECTROMETER STANDARDIZED WITH D20-0 AND D20-100 (#85 BASE OIL) STANDARDS

19 January 1979

Spectrometric Analysis

	Fe	Ag	Al	Be	Cr	Cu	Mg	Na	Ni	Pb	Si	Sa	Ti	B	Ba	Cd	Mn	Mo	V	Zn
D20-3																				
X, ppm	3.15	3.14	3.67	2.65	2.93	2.94	4.04	2.73	1.92	2.61	2.85	3.50	3.03	4.03	2.95	2.93	3.02	3.89	2.77	2.97
σ, ppm	0.13	0.20	0.38	0.21	0.33	0.21	0.23	1.06	0.64	0.20	0.16	0.46	0.20	0.38	0.13	0.25	0.20	0.07	0.99	0.15
σ, percent	4.3	6.5	10.3	7.9	11.3	7.2	5.7	38.9	33.5	13.0	5.5	13.3	6.5	9.5	4.5	8.4	6.5	1.76	35.9	5.0
D20-10																				
X, ppm	9.71	10.16	10.81	9.55	9.56	10.02	11.07	9.93	8.73	8.87	9.38	9.81	9.90	10.34	10.29	9.83	10.11	9.92	9.59	9.20
σ, ppm	0.31	0.18	0.15	0.28	0.2	0.15	0.40	0.07	0.55	0.32	0.41	0.47	0.51	0.33	0.21	0.34	0.29	0.44	0.53	0.61
σ, percent	3.1	1.7	1.4	3.0	1.2	1.5	3.4	0.7	6.3	3.63	4.4	4.8	5.1	3.2	2.0	3.5	2.9	4.4	6.2	6.6
D20-50																				
X, ppm	47.64	49.24	48.04	47.47	49.46	49.29	48.79	50.90	48.63	46.09	46.16	46.84	44.91	44.03	46.26	45.58	47.98	45.73	47.73	42.55
σ, ppm	1.61	1.87	1.27	1.75	0.92	1.46	1.65	1.26	1.29	0.83	1.90	1.55	2.13	1.15	1.07	1.51	1.46	2.82	1.14	2.61
σ, percent	3.4	3.8	2.6	3.7	1.9	3.0	3.4	2.5	2.6	1.8	4.1	3.3	4.7	2.6	2.32	3.3	3.0	6.2	2.4	6.1

SUMMARY OF DATA

19 January 1979

Spectrometric Analysis																			
Fe	Ag	Al	Be	Cr	Cu	Hg	Na	Ni	Pb	Si	Sn	Ti	B	Ba	Cd	Mn	Pb	V	Zn
D20-100																			
\bar{x} , ppm																			
93.7	93.7	95.9	94.2	96.4	96.4	94.4	97.1	97.3	95.7	93.6	95.2	92.4	83.7	94.5	94.2	94.2	92.2	96.2	82.5
σ , ppm																			
1.17	2.41	1.65	1.27	0.82	1.01	1.47	1.07	2.10	1.63	1.89	1.25	2.09	2.47	1.20	1.27	1.45	3.43	1.83	1.78
σ %, percent																			
1.2	2.6	1.7	1.3	0.9	1.0	1.6	1.1	2.2	1.7	2.01	1.3	2.3	3.0	1.3	1.3	1.5	3.7	1.90	2.2
D20-500																			
\bar{x} , ppm																			
97.3	97.0	99.9	97.4	100.1	98.4	98.1	100.8	99.8	100.0	97.8	98.3	106.4	101.2	98.3	98.0	97.9	96.8	100.4	91.3
σ , ppm																			
1.61	3.05	1.94	1.77	1.78	1.84	2.37	6.18	3.52	1.95	1.40	1.56	2.75	2.21	0.75	1.72	2.04	3.51	3.53	7.46
σ %, percent																			
1.7	3.1	1.9	1.6	1.6	1.9	2.4	6.1	3.5	1.9	1.4	1.6	2.6	2.2	0.8	1.8	2.1	3.6	3.5	9.2

SECTION IV
EVALUATION OF PLASMA SPECTROMETERS FOR
THE OIL ANALYSIS PROGRAM

1. INTRODUCTION

Oil analysis is a technique which monitors wear within the equipment's oil-wetted system by determining the concentration of wear metals in samples of the equipment's lubricant. The wear metals are generated by the moving surfaces of the metallic components within the lubricated system. Wear metal analysis coupled with knowledge of the metallurgy of oil wetted components allows one to identify the wearing component and replace it before failure occurs.

The most commonly used analogies involve the medical profession where the lubricant can be compared to a patient's body fluids. A physician can pinpoint abnormalities within the human body by having body fluids analyzed. Likewise, abnormalities within a turbine engine can be identified by analyzing the lubricants.

The United States Air Force initiated an oil analysis program in the mid 1960's in order to monitor wear in aircraft engines. To date, the Oil Analysis Program (OAP) has been successful in improving fleet reliability and readiness. The program accomplishes its goal by detecting abnormal wear before serious damage occurs. Since engines are overhauled only when abnormal wear is indicated by oil analysis, significant savings in maintenance costs have also been realized. Although the success of the oil analysis program cannot be questioned, there are still hundreds of engines that fail every year without any prior indication of abnormal wear by currently used oil analysis techniques.

Within the oil wetted system, chemical reactions and mechanical interactions can occur which result in engine failure.

When wear mechanisms such as fatigue, adhesion and abrasion occur, metallic particles will be generated. The generated particles are very detrimental and often accelerate wear by degrading component surfaces.⁽¹⁶⁾ Therefore, analytical techniques which detect particles are desired.

Due to the different types and degrees of wear, the generated wear metal particles may range from submicrometer to millimeter in size. Although the small particles ($< 1 \mu\text{m}$) produced by normal rubbing wear are quantitatively analyzed by the A/E35U-3 and AA spectrometers, both spectrometers are blind to particles larger than 3-10 μm .⁽¹⁷⁾ This fact allows wear mechanisms which produce large particles to proceed undetected. In such cases the engine will fail with no prior indication from oil analysis.

Such cases have been documented by the Army OAP⁽¹⁸⁾ where large particles were not analyzed by the A/E35U-3 spectrometer and unpredicted engine failure occurred. Therefore, the breakdown of OAP in predicting imminent engine failure can be related, in some cases, to the particle size detection limits of the A/E35U-3 and AA spectrometers. It is because of this fact that the present work was initiated by the Materials Laboratory and supported by the PRAM Program Office.

This effort involved evaluating two state-of-the-art plasma emission spectrometers. Because of their high temperature (10,000 $^{\circ}\text{K}$) plasma sources, they were expected to quantitatively analyze wear metal particles and improve the Oil Analysis Program's ability to predict imminent engine failure.

The evaluation of the plasma spectrometers was carried out in two phases. Phase I dealt with evaluating the capabilities of the plasma spectrometers as they were received from the manufacturer. The capabilities and limitations of the plasma source spectrometers, as well as those of the currently used OAP instruments, were determined and comparisons made.

The results of the Phase I evaluation were disappointing. Every emission instrument evaluated could not quantitatively analyze particles larger than 3-10 μ m. The inefficiency of each instrument's sample introduction system was identified as the reason each instrument failed to achieve its expected potential. At this point, Phase II was initiated in order to improve the sample introduction systems for the plasma emission spectrometers. Improvement of the sample introduction systems would improve the efficiency of particle transport, and in turn, improve the particle detection capabilities of the plasma emission spectrometers. The results are in the report⁽¹⁹⁾, and are only summarized herein.

2. FINDINGS

The two plasma emission spectrometers evaluated were the SMI-III manufactured by Spectrametrics, Inc. and the FAS-2PL manufactured by Baird Atomic, Inc. The SMI-III incorporates a three electrode direct current plasma source while the FAS-2PL uses a radio frequency inductively coupled plasma source.

a. Phase I

Phase I of the program began immediately after the instruments were received and installed. The SMI-III was initially equipped with a two electrode direct current plasma source. The two electrode source never achieved the stability required for accurate wear metal analyses and was replaced with the three electrode direct current plasma jet within the project's first few months.

Before the project began, we anticipated the need for an accurate method which could be used to determine the true concentration of wear metal in oil samples. Without such a method, the effectiveness of spectrometric methods could not be determined, since they would have no common base for

comparison.

A method was successfully developed and its accuracy verified on used MIL-L-7808 lubricants as well as on metal particles suspended in oil. The metal particle suspensions were prepared from -325 mesh (average particle size of 44 μm) and -200 mesh (average particle size of 74 μm) metal powders. The optimum method involves adding a small amount of an acid mixture to the oil and ultrasonically agitating the oil-acid mixture for 45 min. at 65°C. The reaction mixture is then diluted with a mixture of isopropyl alcohol and methy isobutyl ketone to give a homogeneous solution suitable for spectrometric analysis. The recoveries for metal particles of Ni, Fe, Mg, Cu, Al, Sn, Mo and Ti ranged from 97 to 103% with relative standard deviations of 4 to 10%.

Historically, the results from the A/E35U-3 and AA instruments have never agreed. This fact has largely been ignored and separate wear metal guidelines were established for each instrument. For this work it was essential that results from both instruments agreed or an accurate assessment of each instruments capabilities could not be made.

A detailed study was undertaken to determine the effects of concomitant elements, oil type and formulation, and standard composition on A/E35U-3 analyses. It was shown that concomitant elements suppress the analyte's emission, ester oils enhance the analyte's emission relative to hydrocarbon oils and standard composition affects instrument calibration. By using Conostan standards prepared in MIL-L-7808 oil and correcting the A/E35U-3 results for interelement interferences the results from the A/E34U-3 agreed with the results from the Perkin-Elmer 305B AA spectrometer.

The next task under Phase I of the effort was to determine the effectiveness of the PE305B, A/E35U-3, SMI-III,

and FAS-2PL for analyzing metallic particles. The capabilities of these instruments were determined by analyzing particles of known sizes which were suspended in MIL-L-7808 oil. The metal particle suspensions were prepared using high purity metal powders. Particle sizes were established by filtering the suspension through 1-, 3-, 5-, 8-, 10- and 12- μm Nuclepore membrane filters. In this manner, filtrates with known maximum particle sizes were obtained and the concentration of metal in each filtrate was calculated.

None of the instruments quantitatively analyzed particles larger than 3-10 μm . However, the SMI-III analyzed particles larger than 5 μm more efficiently than the other instruments and can quantitatively analyze $< 3 \mu\text{m}$ particles for all metals except Mo. The A/E35U-3 gave the next best results. The results indicated that the A/E35U-3 can analyze 10 μm Mg particles. For other elements the results were not encouraging and the A/E35U-3 cannot quantitatively analyze metallic particles larger than 1-3 μm . The FAS-2PL and the PE305B gave comparable results and neither instrument can quantitatively analyze particles larger than 1-3 μm .

These results were disappointingly low for all of the instruments. An investigation into the particle transport processes revealed that particles were not being efficiently transported to the sources where they could be analyzed. This fact later led to the investigations undertaken during Phase II.

The Fe metal particle suspension was also analyzed using the PE305B fitted with a graphite furnace atomizer (HGA-2100). In this case, the sample is directly pipetted into a graphite tube which is electrically heated to vaporize the sample. The vaporized sample is then detected using atomic absorption methods. The results obtained for this method were encouraging. Although the temperature never is higher than 2800° the method was capable of quantitatively analyzing 20-30

μm iron particles. This fact indicates that if the transport efficiency is improved (and the residence time increased) 20-30 μm particles can be analyzed by sources with temperatures of 2800°C or higher.

The instruments were also evaluated by analyzing several hundred used turbine engine lubricants. The concentrations determined by each instrument were compared with the results from the PSIM. The comparison revealed that the SMI-III and the FAS-2PL analyzed the wear metals in used lubricants effectively.

No significant difference between the various instruments was noticed for the majority of used lubricant samples. However, the SMI-III consistently analyzed the samples containing particles more effectively than the other instruments.

The HGA-2100 graphite furnace was used to analyze some of the samples and again it was able to quantitatively analyze the Fe in all used lubricant samples tested. However, it must be remembered that the HGA is an atomic absorption method and has all the disadvantages associated with the PE305B.

b. Phase II

An investigation into the sample introduction systems employed on the plasma instruments revealed that the particles were not being efficiently transported to the plasma sources. Therefore, the efficiencies of various nebulizers and nebulizer/spray chamber combinations were determined so that a more efficient sample introduction system could be designed.

The optimum sample introduction system was designed by combining the ceramic nebulizer and a glass cylindrical spray chamber (no baffle). This system can quantitatively transport particles less than 7 μm and ~ 60% of the particles of sizes between 7 and 14 μm to the source. However, the system can transport only 11% of the particles with sizes between 14 and 28 μm .

The above sample introduction system was used to analyze the iron particle suspension. The results showed that the direct current plasma source can analyze 100% of the particles less than 14 μm and $\sim 70\%$ of the particles between 14 and 28 μm that are transported to the source. The weak link in the system is still the sample introduction system but the possibility of designing an even more efficient system seems remote at this time.

The ceramic nebulizer/glass cylindrical spray chamber was also tested on the FAS-2PL. Improvements in the FAS-2PL's particle detection capabilities were also evident but particles larger than 14 μm were not analyzed effectively. The rather low argon gas flow rate used to transport the sample to the torch is probably the reason that larger particles are not detected.

The ceramic nebulizer/PE cylindrical spray chamber was also incorporated into the PE305B. An improvement in the PE305B's particle detection capabilities was also evident, especially when the observation height was adjusted to maximize the absorbance from metal particles.

The sample introduction system of the A/E35U-3 was not extensively investigated. Originally, it was thought that the system was relatively efficient since the sample is directly transported to the source by the rotating disk electrode. Recently, samples were collected from the rotating disk and examined for particles. No particles larger than 10 μm were found and very few particles larger than 5 μm were observed in the collected sample. These results indicate that the particle detection capabilities of the A/E35U-3 are also limited by its sample introduction method.

During Phase II the size of wear metal particles found in used lubricating oils was also determined. The particles found in samples from T⁶ engines were examined by an optical microscope and the particle size distribution was determined

by using filtering techniques. Samples from engines which failed undetected by OAP contained wear metal particles larger than 10 μm and 26% of the wear metal was contained in particles larger than 5 μm .

Special samples were collected during Phase II of the work. Representative engines in the Air Force's fleet were monitored and the oil samples saved. If any engine being monitored failed undetected by OAP the oil sample after failure and the 4 samples collected prior to failure were analyzed and examined for particles.

Only seven special failure samples were received. Although some of the samples contained particles the data set was not large enough to draw any conclusions.

3. CONCLUSIONS

We have shown that the SMI-III coupled with the ceramic nebulizer/cylindrical glass spray chamber detects larger particles than the original SMI-III system (Varian nebulizer/plastic diamond spray chamber). When the plasma is optimized for the analysis of particles the instrument can analyze particles as large as 14-20 μm . Even when the instrument is operated with the ceramic nebulizer/plastic diamond spray chamber at optimum sample uptake rate and nebulizing gas pressure, the particle detection capabilities of the SMI-III are superior to currently used OAP spectrometers.

The only spectrometric method superior to the SMI-III is to utilize a nonflame atomizer in an atomic absorption instrument. The HGA-2100 graphite furnace atomizer gave 100% recoveries of Fe particles less than 30 μm . However, nonflame atomic absorption is not a multielement analytical method and carries with it the disadvantages associated with the atomic absorption determination of wear metals.

Although the FAS-2PL did not score high marks in its particle detection capabilities it has provided adequate analyses of wear metals in used lubricating oils. Only in samples which contained very high concentrations of particles did the FAS-2PL give significantly lower results than the SMI-III.

The particle detection capabilities of the A/E35U-3 were also lower than expected. An examination of the particle transport capabilities of the rotating disk has revealed that large (5-10 μm) particles are not being transported to the arc/spark source. Therefore, it is assumed that slight modifications of the sample introduction system⁽²⁰⁾ for the A/E35U-3 would improve its particle detection capabilities.

The particle detection capabilities of the atomic absorption method can also be improved by judicial adjustment of the observation height and removal of the flow spoiler. By increasing the analyte's residence time, particle detection capabilities of the PE305B approach those observed for the emission instruments.

During the course of this work a particle size independent method was developed. The particle size independent method coupled with direct analysis can be used to detect the presence of metallic particulate contamination. The method proposed would be easier to use and to interpret than a Ferrographic analysis.^(21, 22) All that is required is to analyze the sample directly and with the PSIM. If the concentrations determined by the two methods differ by more than 30%, the sample contains a significant concentration of particles and abnormal wear should be predicted.

Ever since the time both atomic absorption and atomic emission instruments were used in the Oil Analysis Program, differences were observed between the wear metal concentrations determined by the two instruments. These differences resulted from matrix and interelement interferences. The A/E35U-3

results agree with the AA results when single element standards are used to calibrate the A/E35U-3 and the standards are prepared in the same oil as the oil being analyzed.

Used oil samples analyzed using the PE305B, SMI-III, and the FAS-2PL were compared. The results showed that the atomic absorption wear metal guidelines could be used for both plasma instruments.

4. RECOMMENDATIONS

According to our work the SMI-III is the best instrument evaluated for the determination of wear metals. However, the SMI-III is not perfect. The largest drawback is that the source is not exceptionally stable and does require frequent calibration. Excluding that one drawback, the instrument is excellent and is easy to operate. Since the grating and plasma height are adjustable there is some operator's skill required in order to maximize the detection of the emission signal. Therefore, we did observe slight variations in concentrations determined by different operators.

This work has shown that a significant improvement in transporting particles to the source can be affected by modifying commercially available sample introduction systems. The need still exists for a totally efficient system that is capable of transporting a representative sample of the lubricant to the analytical source. Therefore, more effort is needed in this area and success will result in further improvements in particle detection capabilities.

During this work we only considered the efficiency of the nebulizer/spray chamber combinations in order to improve the particle detection capabilities of the plasma spectrometer. The sample introduction system on the A/E35U-3 was not examined nor were possible improvements envisioned until recently. Several papers have been published⁽²⁰⁾ which suggest that

improvements in the A/E35U-3's particle detection capabilities can be made. An investigation should be carried out to examine the sample transport efficiency of the A/E35U-3 and possible improvements evaluated before any final recommendations are made.

Since the graphite furnace atomizer is the only source which successfully analyzed 20-30 μm particles the obvious conclusion would be to incorporate it into a multielement instrument. This has been accomplished in a few laboratories by incorporating the graphite furnace atomizer into a Spectra-metrics echelle grating spectrometer. Published papers indicate that as many as 16 elements have been successfully analyzed simultaneously by this technique.⁽²³⁾

Since this work began, a new instrument has appeared on the market. This instrument utilizes a graphite braid to transport the sample to a dc plasma source. If a representative sample can be deposited on the graphite braid, this system may provide very good detection of particles. At any rate the instrument deserves evaluation before any new OAP spectro-metric method is adopted.

This work was based on the assumption that the wear metal particles need to be quantitatively analyzed in order to accurately predict abnormal wear. This assumption was addressed in this work by collecting used oil samples from representative turbine engines in the Air Force's inventory. These engines were monitored and the last five consecutive OAP samples were saved. If any of these engines failed, the sample taken after failure and the samples saved prior to failure were analyzed and the particle size distribution of wear metal determined. The objective was to determine the size of wear metal particles present in used lubricating oils that OAP spectrometers should be required to analyze. This question must be answered before the particle detection

capabilities of OAP spectrometers can be specified. More work is required in this area, since no definitive conclusion could be reached due to the small number of samples received during the course of this program.

SECTION V

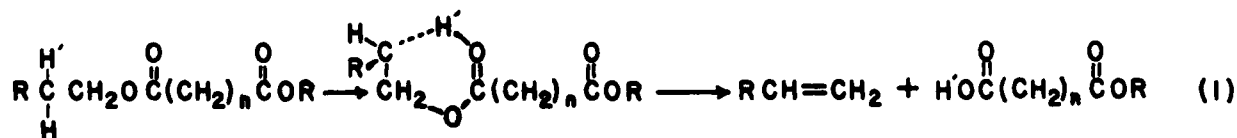
CHEMICAL NATURE OF WEAR DEBRIS

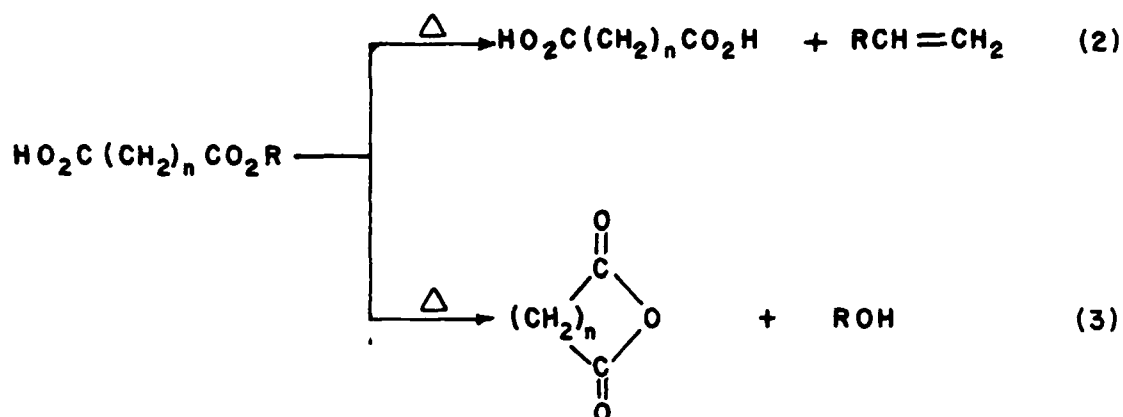
1. INTRODUCTION

An investigation into the chemical nature of Fe, Mg and Cu wear debris in used lubricating oils has been completed. Knowledge of the chemical nature of wear debris is important because it indicates the type and degree of wear occurring in the engine and it affects the efficiency with which the wear debris is analyzed by spectroscopy. The wear debris can be free metal (mechanical wear), metal oxide (oxidative corrosion), or organometallic (chemical corrosion) in nature and can be in the form of dissolved species or suspended particles.

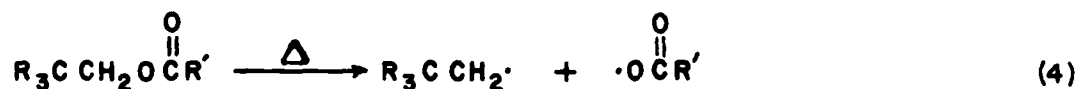
One primary mechanism of wear metal production is corrosion. Corrosion involves a reaction between chemicals in the surrounding fluid and the component surface. The reaction products formed at the component surface are dissolved by the surrounding lubricant or removed as particles through abrasion. Dissolved oxygen in the lubricant reacts with component surfaces to form metal oxides while thermal and hydrolytic decomposition products of the ester base stock and extreme pressure additives react with metal surfaces to form organometallic compounds.

Synthetic ester lubricating oils are primarily based on dibasic acid esters, $RO_2C(CH_2)_xCO_2R$, or neopentyl polyol esters, $R_nC(CH_2O_2CR)_{4-n}$ (where $n = 0-2$). Both classes of ester undergo thermal decomposition at elevated temperatures. At high temperatures the dibasic acid esters undergo an intramolecular rearrangement to form a dicarboxylic acid and two alkenes, as in equation (1) plus (2) or an anhydride alcohol, and alkene as in equation (1) plus (3) (24,25,26).

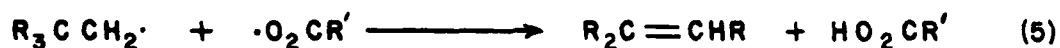




The neopentyl polyol esters are more thermally stable than the dibasic esters. Since the neopentyl polyol ester lack the beta H (H' eq 1) on the alcohol portion of the ester, they decompose via a free radical mechanism to produce carboxylic acids, alkanes, alkenes, and/or peroxides. (24,26)



where R may be alkyl or ester



one possible recombination

Both classes of esters undergo hydrolysis to produce a carboxylic acid and alcohol at about the same rate (26).



For both classes of esters, decomposition (thermal and hydrolytic) produces corrosive products, carboxylic acids and anhydrides, which are capable of reacting with metal surfaces and metal particles to form organometallic species.

The extreme pressure additives present in the ester lubricants are also capable of undergoing thermal and hydrolytic decomposition to produce corrosive compounds, such as phosphate esters (26) $(R-CO_2)_3P=O$, which decompose to form corrosive phosphoric acid, alkenes, and alcohols.

The investigation into the chemical nature of Fe, Mg, and Cu wear debris found in used lubricating oils was divided into three separate stages. In the first stage organometallic species, dissolved and particulates, were produced by heating MIL-L-7808H and MIL-L-23699 synthetic ester oils with metal and metal oxide powders of Fe, Mg, and Cu. In the second stage procedures were developed capable of determining the chemical nature of Fe, Mg, and Cu wear debris. Each procedure was evaluated by employing metal powders, metal oxide powders, and the previously prepared organometallic compounds to simulate wear debris. In the final stage of the investigation the developed methods were used to determine the chemical nature of wear debris in used aircraft lubricating oils.

2. FORMATION OF ORGANOMETALLIC DEGRADATION PRODUCTS

a. Introduction

The first stage of this investigation was to produce organometallic compounds by heating MIL-L-7808H and MIL-L-23699 synthetic ester oils with metal powders and metal oxide powders to $\sim 240^\circ\text{C}$. The organic lubricant decomposition products were identified in order to obtain a better understanding of the lubricant decomposition taking place in the presence of metal particles. Reactions were also carried out using oil without additives (ester base stock in place of MIL-L-7808H) and/or metal powders to identify the effect of each on the decomposition

process. Mobil MIL-L-7808 ester oil was studied first since it has a lower decomposition temperature and is less complicated than Mobil MIL-L-23699.

b. Experimental

(1) Organometallic Standards

Three sets of standards with concentrations of 3000, 1000, 500, 100 and 50 ppm were prepared from Conostan metallo-organic alkyl aryl sulfonate concentrates by diluting with the appropriate amount of Mobil MIL-L-7808 ester oil, Mobil MIL-L-23699 ester oil, or di(2-ethylhexyl) azelate. These were diluted 1:4 (oil:solvent) with MIBK before use. Three sets of blanks were also prepared by diluting Mobil MIL-L-7808 ester oil, Mobil MIL-L-23699 ester oil, and di(2-ethylhexyl) azelate 1:4 with MIBK.

(2) Oil Degradation Procedure

Approximately 100 grams of an oil (MIL-L-7808H or 23699) or ester (di(2-ethylhexyl) azelate) sample and the metal powder or metal oxide to be studied were directly weighed into a 200-ml round bottom flask fitted with a ground glass joint. A magnetic stirrer was placed in the flask. The flask was closed with a ground glass stopper and placed on a heating mantle. The sample was heated to 240°C. The sample was maintained at 240°C with stirring (to keep the metal powder suspended) for 30 and 8 hrs for MIL-L-7808H and MIL-L-23699, respectively. The sample was cooled to room temperature and particles allowed to settle. The liquid portion of the sample was then decanted, centrifuged 10 min, decanted again, and the liquid filtered through a 0.6 μ m filter to remove any remaining undissolved metal species.

The liquid obtained above was analyzed on a Hewlett Packard 5830A gas chromatograph equipped with a 18850A terminal (conditions are listed in Table 51) to separate the decomposition products. The SMI-III was used (after diluting

TABLE 51
OPERATING CONDITIONS FOR GAS CHROMATOGRAPH

<u>Parameter</u>	<u>Conditions</u>
Column	3% Dexsil 400 on 80/100 Chromosorb W, glass 0.08-in. ID, 0.25-in. OD, 6 ft long
Sample	0.1 μ L (neat)
Flow rate	20 mL/min He
Inlet Temp	250°C
FID Temp	375°C
Chart Speed	1.00 cm/min
Temp Program Parameters	
MIL-L-7808	
Temp Range	20-350°C
Rate	15°C/min
Time 1	2 min
Time 2	5 min
MIL-L-23699	
Temp Range	180-350°C
Rate	1.5°C/min
Time 1	5 min
Time 2	10 min
MIL-L-23699 (Degradation Products)	
Temp Range	35-200°C
Rate	1.0°C/min
Time 1	6 min
Time 2	15 min

the liquid 1:4 with MIBK) to detect the presence of dissolved metal species.

The liquid was distilled at atmospheric pressure to separate the volatile decomposition products (BP < 240°C) from the undecomposed oil or ester and the nonvolatile decomposition products (BP > 240°C). The isolated volatile compounds were then examined using gas chromatography, infrared spectroscopy and mass spectroscopy. The infrared spectra were obtained with a Perkin-Elmer 521 spectrometer and the mass spectra were obtained on a Dupont 21-491B mass spectrometer equipped with a Finnigan data system. Distillate fractions (1 atm) were collected from the MIL-L-7808 reactions at 115-121, 180-190 and 200-240°C.

The nonvolatile liquid (liquid remaining after distillation) was washed with 1 M NaOH solution to extract any remaining carboxylic acids or anhydrides. The washings were separated from the organic phase and neutralized with acid. The resulting organic layer was then separated from the aqueous phase, dried over Na_2SO_4 and examined by infrared spectroscopy.

The solid material collected on the filter and remaining in the round bottom flask were combined and washed with pentane to remove any remaining thermally decomposed oil or ester. The solids were placed in an Erlenmeyer flask and treated several times with ethanol in an attempt to dissolve the organometallic species and separate the organometallic compounds from the non-reacted metal powder. The washings were combined, centrifuged for 10 min, the liquid portion decanted, and the liquid diluted with pentane. Upon dilution with pentane a precipitate formed which was collected by filtration and washed with pentane. One portion of the solid was submitted to the Micro Analytical Lab (AFWAL/MLU) for C, H and P analysis, another was dissolved in aqua regia for metal analysis on the SMI-III, a third portion was studied by infrared spectroscopy as

a KBr pellet, and a fourth portion was studied by HNMR spectroscopy (Varian A-56/60 A analytical spectrometer as $d\text{-CF}_3\text{CO}_2\text{D}$ or $d\text{-CDCl}_3$ solution).

c. Results and Discussion

(1) Thermal Degradation of MIL-L-7808H Lubricants

The unreacted Mobil MIL-L-7808H ester oil and di(2-ethylhexyl) azelate were analyzed by gas chromatography (Figure 12) and found to be identical in composition (the additives were not observed). The oil and ester are not a single compound but actually a mixture of various high boiling 2-ethylhexyl esters, a fact which complicates the identification of decomposition products and organometallic species.

The gas chromatogram (Figure 13) produced by the ester or oil heated to 240°C without metal present had peaks with retention times (min) in the ranges 1.20-1.50 (2 peaks, 1 major and 1 minor), 5.40-6.80 (2 peaks, 1 major and 1 minor), 8.80-13.20 (6 peaks), and 14.30-27.30 (20-30 peaks). The unheated oil and ester possessed peaks only in the 14.30-27.30 range (Figure 12). Therefore, the very complex region from 14.30-27.30 is due to the various high boiling esters and was ignored when studying decomposition products.

The heated oil was distilled and the fraction distilling at $115\text{-}121^\circ\text{C}$ (atmospheric pressure) was collected. The collected fraction was injected into the GC and the compounds present had retention times between 1.2 and 1.5 min. A mass spectrum of the volatile fraction gave a molecular ion of 112 atomic mass units. The infrared spectrum (Figure 14) contained absorption peaks at 3050, 1650 and 885 cm^{-1} all indicative of an alkene with a structure of $\text{HC}_2=\text{CR}_2$. The data is consistent with an alkene with the formula C_8H_{16} . Therefore, the major compound with GC retention time of 1.28 is most likely 2-ethyl-1-hexene (B.P. = 120°C) as predicted from equation (7).

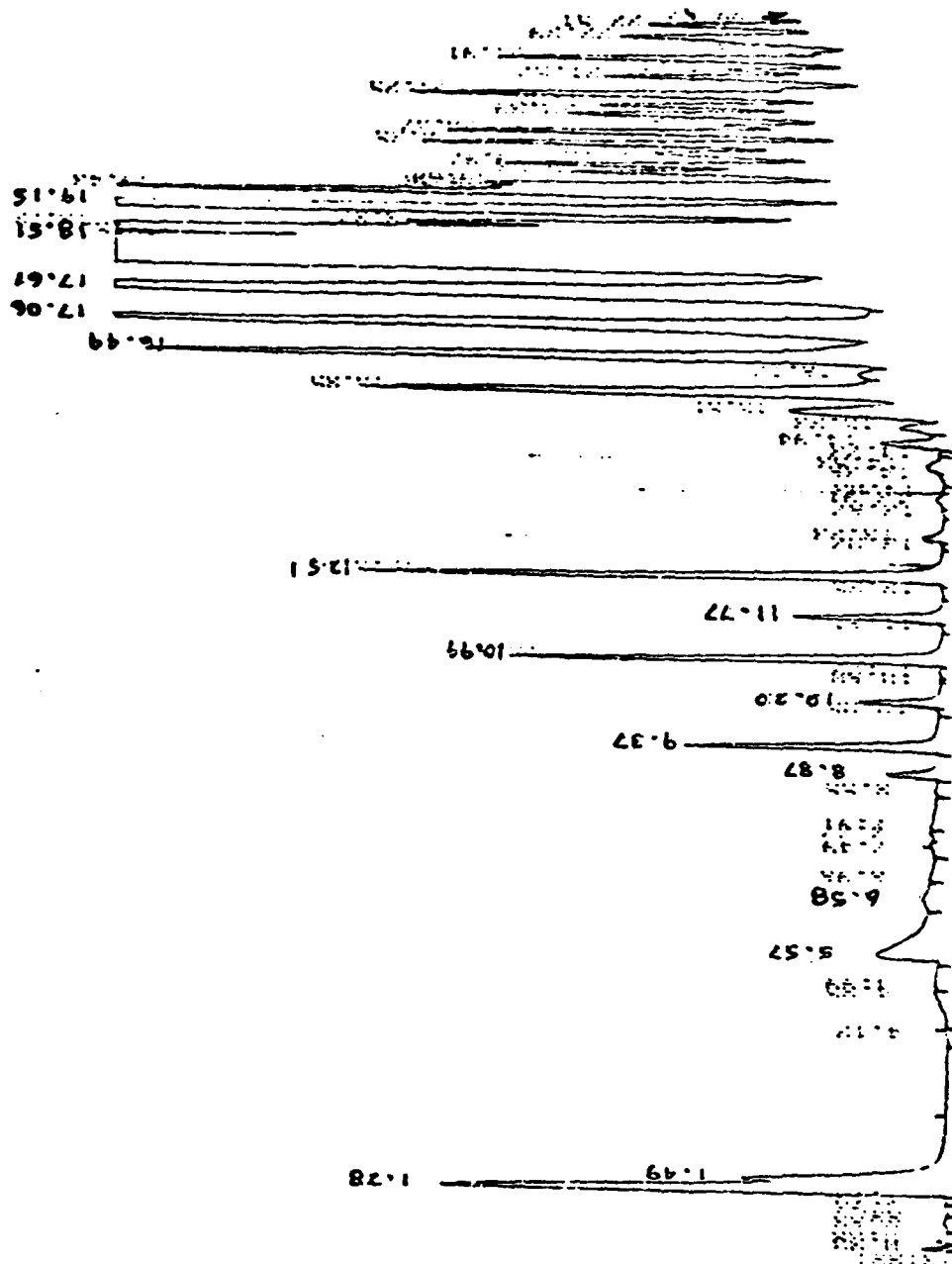


Figure 13. Gas Chromatogram of Mobil MIL-L-7808H or Di(2-ethylhexyl) azelate After Heating at 240°C for 30 hrs.

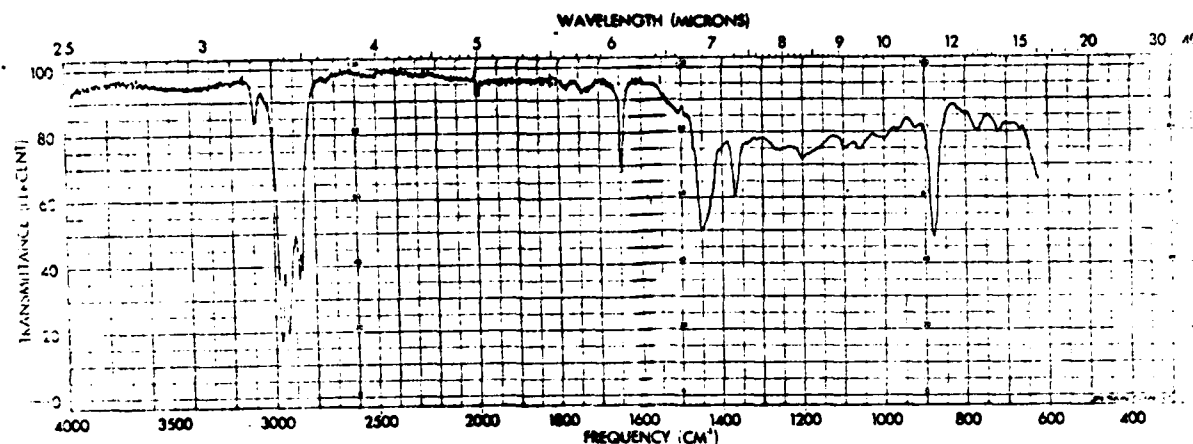
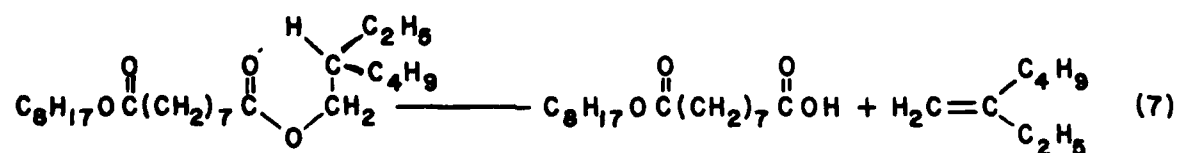


Figure 14. Infrared Spectrum of 2-Ethyl-1-Hexene



The minor GC peak seen at retention time of 1.49 is most likely an isomer due to the thermal rearrangement of 2-ethyl-1-hexane.

The peaks which appeared at 5.40-6.80 min in the gas chromatogram (Figure 13) were identical to those obtained for the distillate fraction collected in a temperature range of 180-190°C. The mass spectrum for the distillate contained a possible molecular ion at $M/e = 130$ mass units. The distillate's infrared spectrum (Figure 15) possessed a strong band at 3360 cm^{-1} indicative of an alcohol.

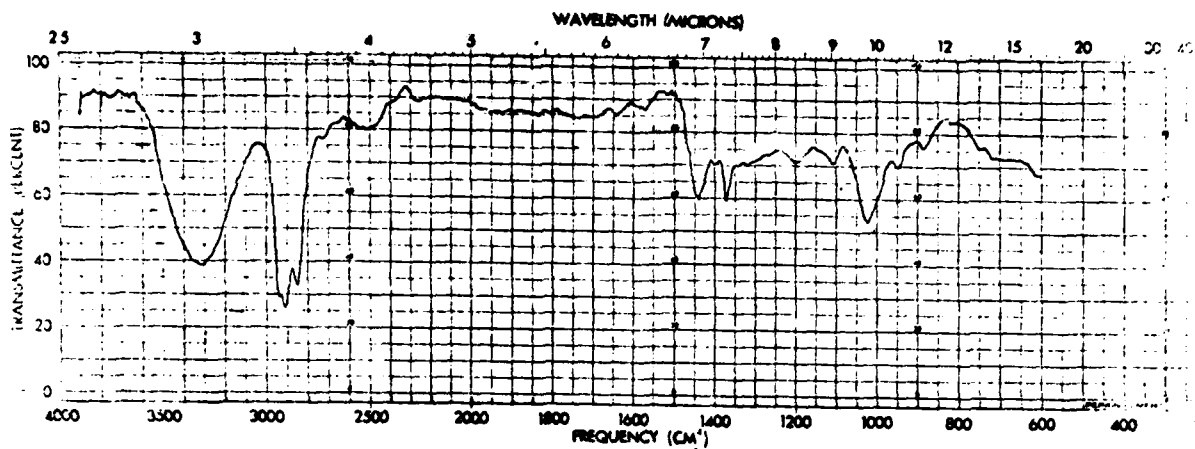
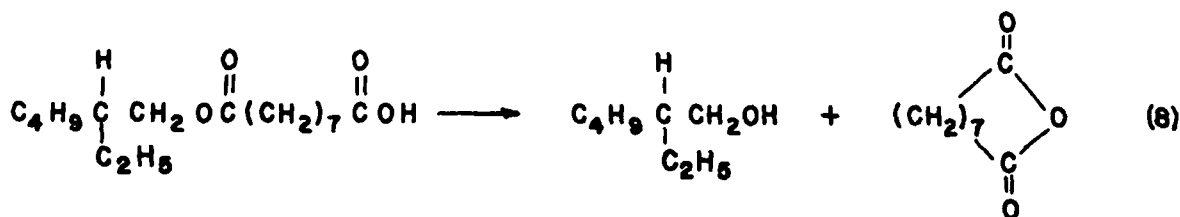


Figure 15. Infrared Spectrum of 2-Ethylhexanol

The formula for an alcohol with M.W. = 130 is $C_8H_{17}OH$. The major compound present is probably 2-ethylhexanol which would be produced by anhydride formation (eq. 8) or hydrolysis (eq. 6).



The fraction which distilled between 200 and 240°C has gas chromatogram peaks in the 8.80-13.18 min range. The mass spectrum of the distillate had major peaks in the range of $M/e = 132$ -205 mass units. The infrared spectrum (Fig. 16) showed a broad, strong band from 3500-2500 cm^{-1} and a strong band at 1700 cm^{-1} indicative of carboxylic acids.

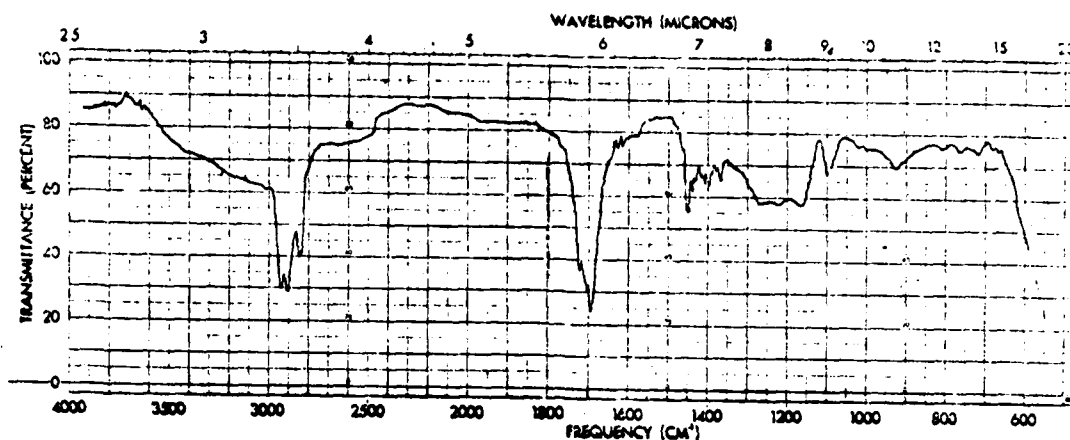


Figure 16. Infrared Spectrum of the 200-240° Distillate Fraction

The nonvolatile compounds, soluble in NaOH also had IR bands indicative of carboxylic acids. The production of alcohols indicates the formation of anhydrides which were not detected by infrared spectroscopy. Any anhydrides present were probably converted into carboxylic acids by moisture in the original ester or oil and by the 1 M NaOH solution used to extract the nonvolatile acids from the decomposed ester. Due to the number of peaks in the gas chromatogram, the carboxylic acids were not identified.

Other compounds found to be present (Figure 13) in trace amounts were 1-hexane, 2-methyl-1-propanol, cyclohexene, and heptane (R.T. = 0.5-1.0 min). 2-Ethyl-hexanal (R.T. = 4.5) probably resulted from the oxidation of 2-ethyl-hexanol and 2-ethylhexyl acetate (R.T. = 8.0).

Therefore, corrosive compounds, carboxylic acids and possibly anhydrides, are produced when the lubricating oil or di(2-ethylhexyl) azelate are heated to approximately 240°C. The metal powder and metal oxide suspensions in Mobil MIL-L-7808H and di(2-ethylhexyl) azelate were then heated to 240°C to observe the effects, if any, of the metal or metal oxide on the decomposition products.

(2) Effect of Metal Powders on the Degradation of MIL-L-7808H Lubricants

The metal powder suspension containing 100 ppm (each metal) of Al, Ag, Cr, Cu, Fe, Mg, Mo, Ni, Pb, Si, Sn, Ti, and Zn was heated to 240°C for 30 hours. After heating, the reaction mixture was analyzed by gas chromatography (Figure 17). Again peaks appeared with retention times (min) in the range 1.20-1.50 (1 peak), 5.40-6.80 (3 peaks, 1 major and 2 minor), and 8.80-13.20 (6 peaks) indicating the presence of 2-ethyl-1-hexene, 2-ethylhexanol, and carboxylic acids.

The only major difference in the gas chromatograms of the heated oil with and without metal present (Figure 13 & 17) was in the ratio of alkene, alcohol and carboxylic acid peaks. In the heated oil or ester the ratio of alkene:alcohol:carboxylic acid was 2:1:4 while the presence of metal produced a ratio of 1:8:32. The ratio of the total & peak area of the decomposition products with retention times of 1.20-13.20 min to the total & peak area of the unreacted esters with retention times of 13.20-27.30 min indicates that the amount of decomposition was almost doubled by the presence of metal.

(3) Effect of Metal Oxides on the Degradation of MIL-L-7808H Lubricants

The metal oxide suspension in oil containing CuO, MgO, Al₂O₃, TiO₂, and Fe₂O₃ was then heated to 240°C for 30 hours. Again the reaction mixture contained alkenes (2 peaks, 1 major and 1 minor), alcohols (2 peaks) and carboxylic acids (6 peaks) but in the ratio of 2:1:11 (Figure 18) as opposed to a ratio of 2:1:4 for the heated oil (Figure 13). The amount of decomposition was only slightly increased by the presence of metal oxides. The reaction mixture was found to contain 40 ppm of a dissolved Cu species. No solid organometallic species were isolated from the reaction mixture.

Therefore, it can be concluded that the presence of metals, and to a lesser extent metal oxides, increases the

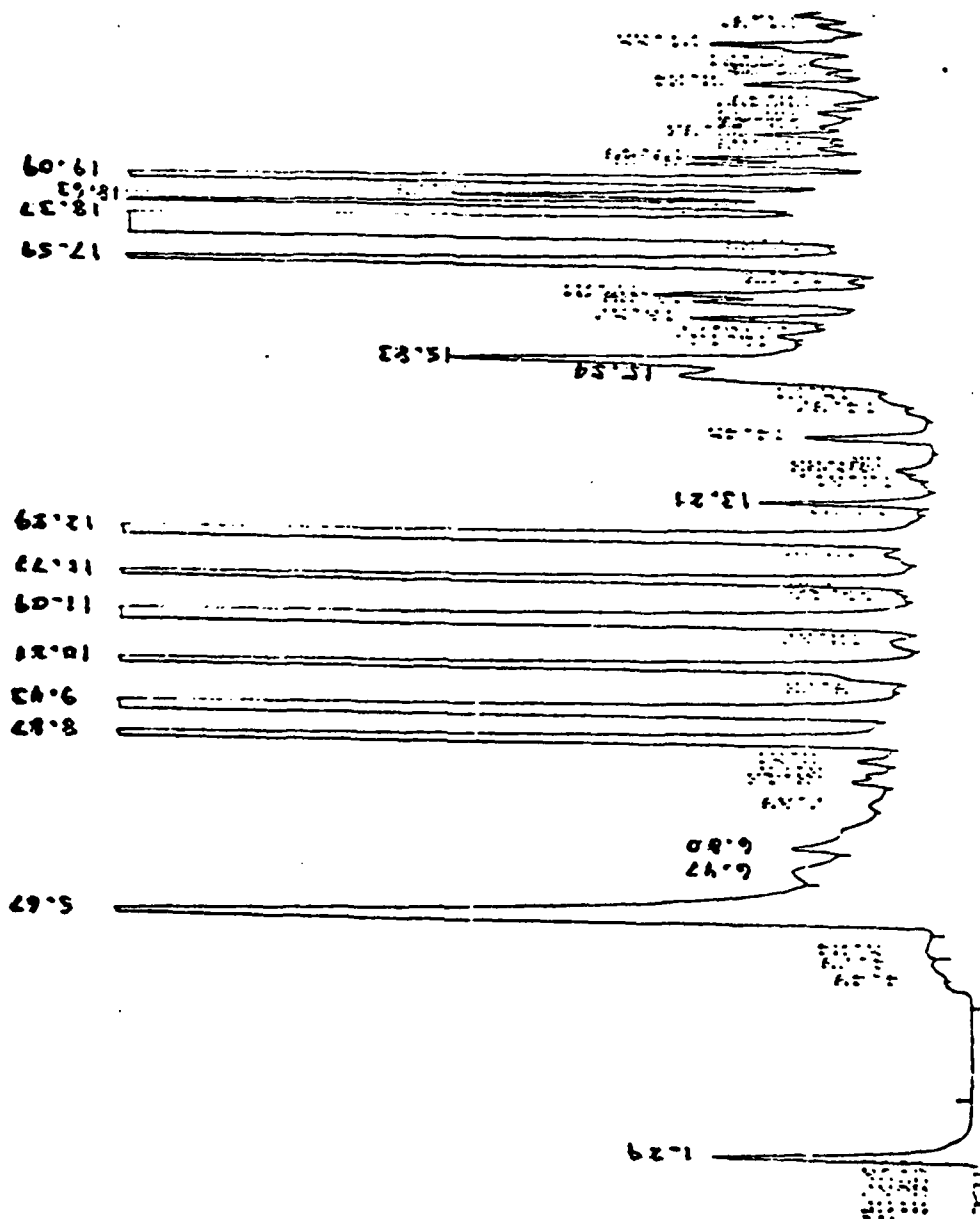


Figure 17. Gas Chromatogram of Mobil MIL-L-7808H after Heating at 240°C for 30 Hrs in the Presence of Metal Powders.

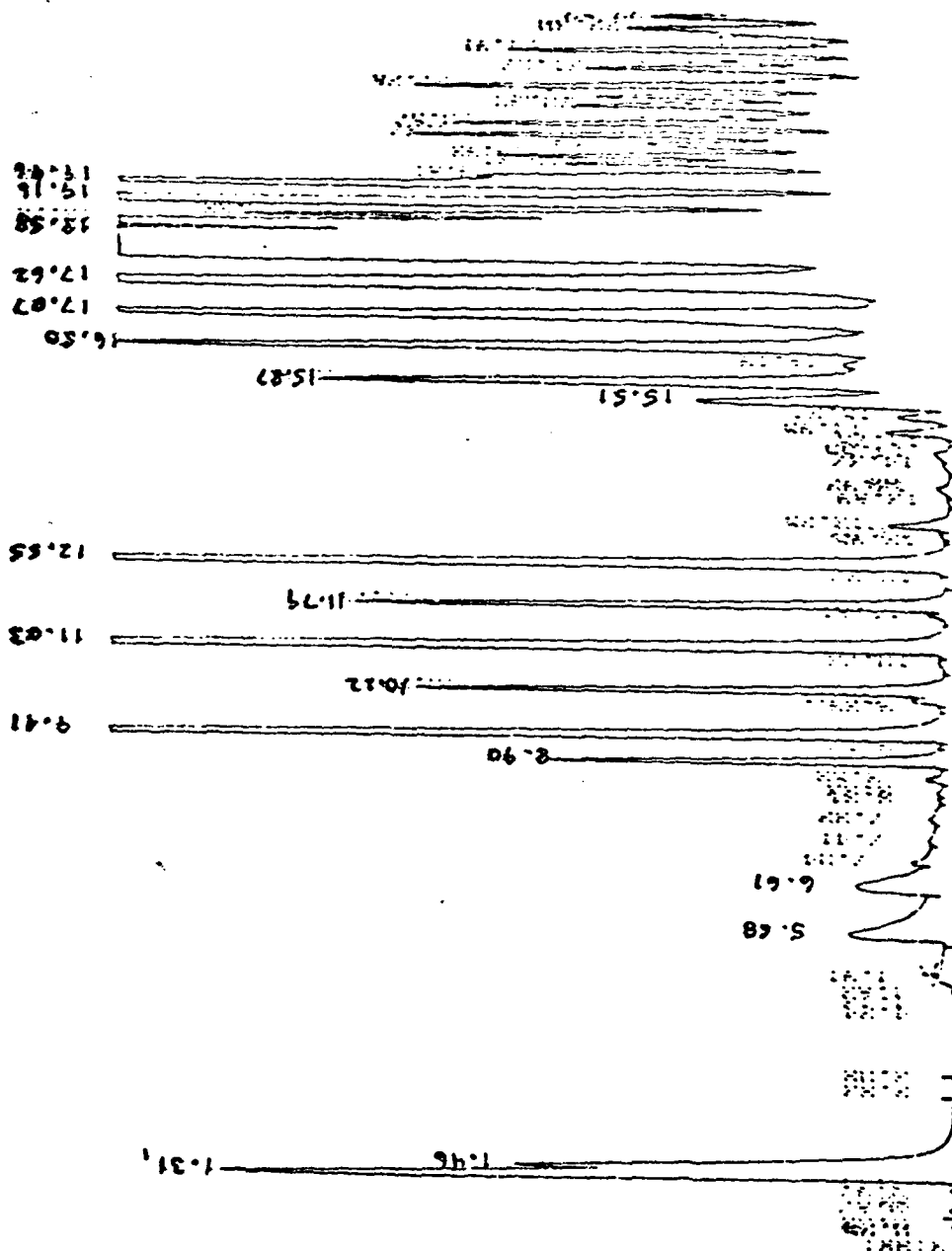


Figure 18. Gas Chromatogram of Mobil MIL-L-7808H after Heating at 240°C for 30 Hrs. in the Presence of Metal Oxides.

degree of decomposition of the lubricating oil. The metals react with the oil decomposition products to form organometallic species which may be dissolved or suspended in the oil.

(4) Isolation and Characterization of Organometallic Degradation Products

Single element suspensions of Zn, Fe, Mg and CuO in Mobil MIL-L-7808H were individually heated to 240°C for 30 hours. To increase the effect of the metal or metal oxide the concentration of metal in each suspension was increased to 2000 ppm. The Zn suspension in Mobil oil produced a liquid fraction containing ~ 1000 ppm of dissolved Zn in addition to alcohols, alkenes, and carboxylic acids. The ratio of alcohol to alkene was 2:1, but the major alcohol and alkene produced were the isomers of 2-ethylhexanol (GC rt = 6.4-6.9) and 2-ethyl-1-hexene (GC rt = 1.49) as opposed to previous reactions in which 2-ethylhexanol (GC rt = 5.6) and 2-ethyl-1-hexene (GC rt = 1.3) were the major products.

A white powder (MP > 250°C) was isolated from the reaction and was found to contain 33.4% Zn, 5.3%P, 37.0%C, and 5.1%H. The remaining 19.2% was assumed to be oxygen. The analytical data affords an empirical formula of $(\text{Zn}_3\text{C}_{18}\text{H}_{30}\text{O}_7\text{P})_x$. The infrared spectrum (Figure 19) of the compound contains a strong band centered around 1560 cm^{-1} and a sharp band at 1730 cm^{-1} . These bands indicate that the compound contains both

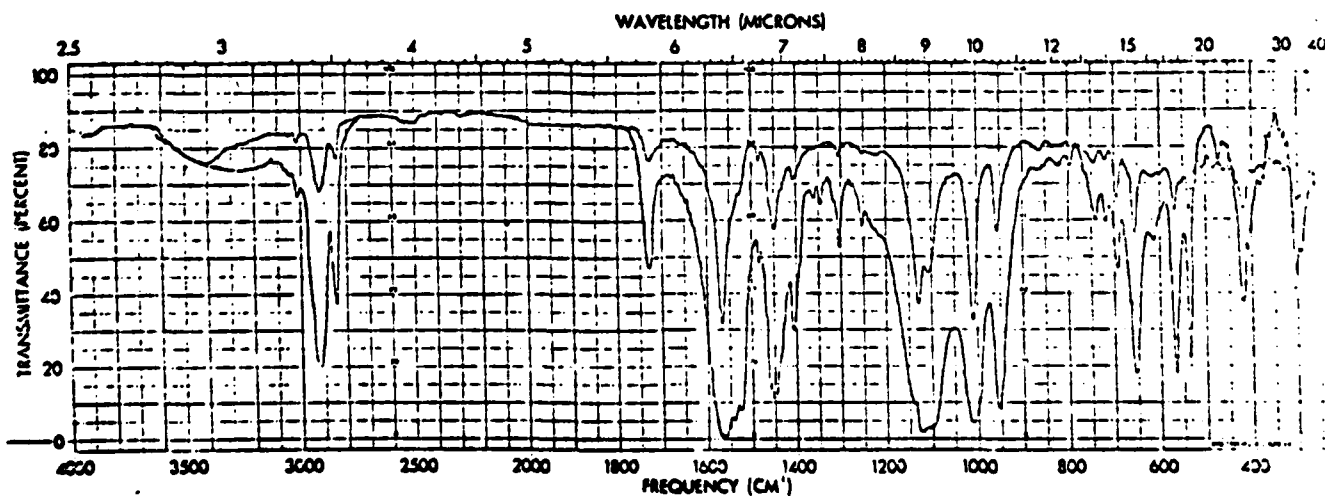


Figure 19. Infrared Spectrum of $[(\text{ZnC}_6\text{H}_{10}\text{O}_2)_3\text{PO}]_x$.

ester and metal carboxylate carbonyl groups. The P content in the isolated product is probably from the reaction of Zn with a phosphate ester additive such as tricresyl phosphate.

A Zn powder suspension (2000 ppm) in di(2-ethylhexyl) azelate was then heated to 240°C for 30 hours. The resulting mixture contained alcohols and alkenes in the ratio 1:3 as opposed to the 2:1 ratio obtained in the Mobil MIL-L-7808 Oil reaction with Zn. The major peaks were due to the 2-ethyl-1-hexene and the isomers of 2-ethylhexanol. The liquid contained 500 ppm of dissolved Zn species. A white powder (M.P. > 250°C) was isolated from the reaction and was found to contain 45.8%C, 6.47%H, 24.5%Zn. The analytical data affords an empirical formula of $(\text{ZnC}_{10}\text{H}_{16}\text{O}_4)_x$. The white powder produces an infrared spectrum (Figure 20) with a strong broad band centered at 1540 cm^{-1} and a sharp band at 1730 cm^{-1} , again indicative of ester and metal carboxylate carbonyl groups. The only major difference between the IR spectrum of the two white solids is that $(\text{ZnC}_6\text{H}_{10}\text{O}_2)_3\text{PO}$ contains three strong bands between $1200\text{--}900\text{ cm}^{-1}$ which $(\text{ZnC}_{10}\text{H}_{16}\text{O}_4)_x$ does not. Therefore, the strong bands from $1200\text{--}900\text{ cm}^{-1}$ are assumed to be due to the phosphorous ester portion of the $(\text{ZnC}_6\text{H}_{10}\text{O}_2)_3\text{PO}$ molecule.

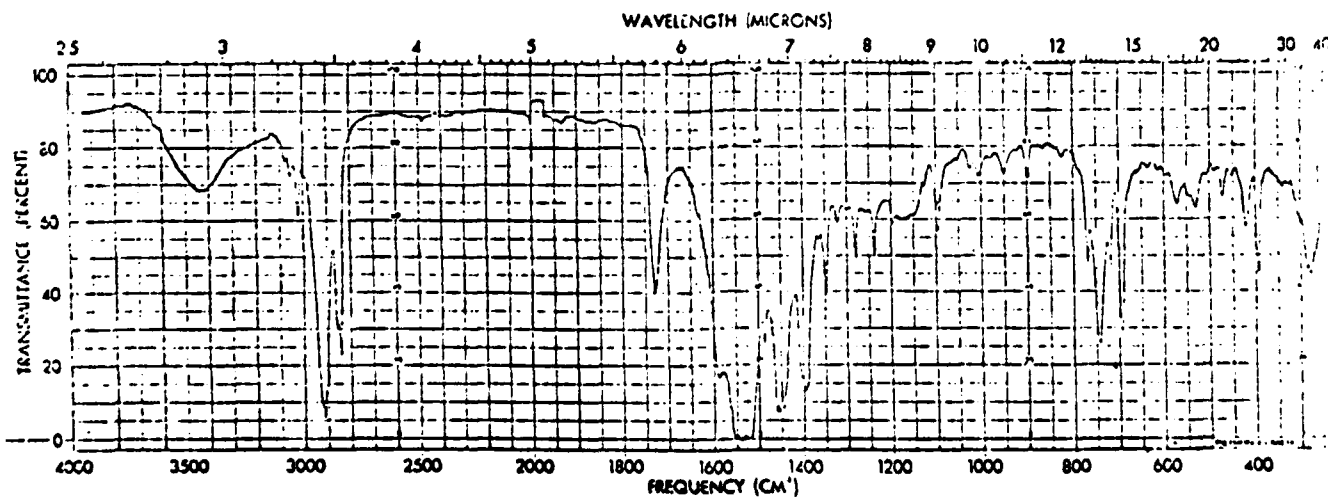


Figure 20. Infrared Spectrum of $(\text{ZnC}_{10}\text{H}_{16}\text{O}_4)_x$.

From the reaction of Zn with Mobil MIL-L-7808 and di(2-ethyl-hexyl) azelate it is apparent that the additives present in Mobil MIL-L-7808 react to form organometallic compounds of higher solubility and affect the production of the decomposition products.

Similarly, when a 2000 ppm Mg suspension in Mobil MIL-L-7808 was heated to 240°C, a reaction mixture containing 2000 ppm of dissolved Mg was produced. The mixture also contained alcohols (isomers of 2-ethylhexanol) and an alkene (2-ethyl-1-hexene) in a ratio 1:2. A solid Mg organometallic could not be isolated even after the Mg concentration was increased to 4000 ppm.

When the 2000 ppm Mg suspension in di(2-ethylhexyl) azelate was heated to 240°C, a liquid containing 80 ppm of dissolved Mg was obtained. The liquid contained only 2-ethylhexanol and 2-ethyl-1-hexene in the ratio 3:1. A tan solid was isolated from the reaction with composition 46%C, 5.7%H, and 13.49%Mg. The tan solid therefore has the empirical formula of $(\text{Mg C}_7\text{H}_{10}\text{O}_4)_x$. The infrared spectrum (Figure 21) contains a strong broad band centered at 1580 cm^{-1} but no bands in the region $1700\text{--}1800\text{ cm}^{-1}$ indicating only metal carboxylate groups are present.

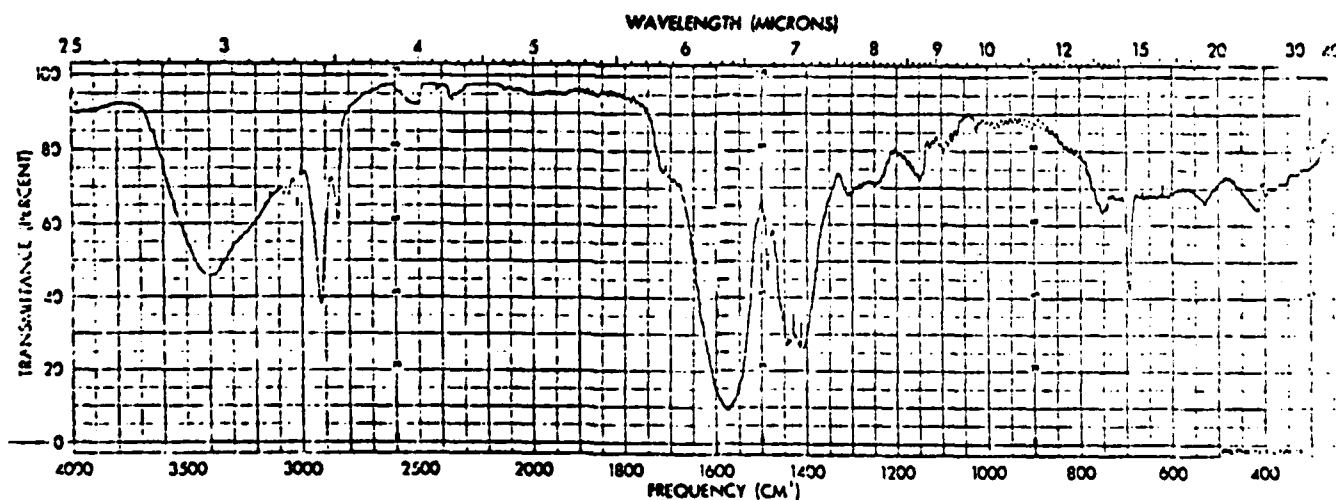


Figure 21. Infrared Spectrum of $(\text{MgC}_7\text{H}_{10}\text{O}_4)_x$

Therefore, the additives present in Mobil 7808 react to form a completely soluble organometallic specie and again the additives affect the thermal decomposition products obtained.

The other metal and metal oxide suspensions, whether in oil or ester, did not produce organometallic solids.

The summary of the metal content and decomposition products found in the liquid fraction of the reacted suspensions is as follows:

	<u>CuO in Ester</u>	<u>CuO in Oil</u>	<u>Fe in Oil</u>	<u>Fe in Ester</u>
Alcohol: Alkene	3:1	1:10	1:2	3:1
Metal Content (ppm)	80	102	465	300

As previously observed, the presence of metal, metal oxide, and additives affect the amount and ratio in which the decomposition products are formed. The additives present react to form more soluble organometallic species.

Therefore, it has been shown that organometallic species, dissolved and undissolved, are formed when an ester lubricating oil is heated to high temperatures in the presence of metal. The presence of metal, especially Zn, Mg and Fe, increases the rate of decomposition of the oil and changes the ratio and variety of decomposition compounds produced. The additives present in the oil react to increase the solubility of the organometallic species formed and also affect the decomposition compounds produced.

(5) Thermal Degradation of MIL-L-23699 Lubricants

The majority of used oil samples received by this laboratory which contain > 5 ppm Mg were MIL-L-23699 oils. Therefore, the reaction of Mg with MIL-L-23699 was investigated. A chromatograph of unreacted Mobil MIL-L-23699 is shown in Figure 22. The antioxidant appears at a retention time (min) of 7.3 and the extreme pressure additive, tricresyl phosphate, appears at retention times from 20.7 to 31.0 min. The oil is a complex mixture of high boiling esters which make the identification

of organic and organometallic decomposition products rather difficult.

The chromatogram of the Mobil MIL-L-23699 after heating at 240°C for 8 hours is shown in Figure 23. Except for the lower amount of antioxidant present, the heated oil appears to be identical with the original oil (Figure 22). The presence of Fe had little effect on the oil although a soluble organometallic species (120 ppm) was produced.

The chromatogram of the Mobil MIL-L-23699 heated with Mg at 240°C for 8 hours (Figure 24) shows that volatile decomposition products have been formed and the supply of antioxidant depleted (RT = 7.3).

After 8 hours (compared to 30 hours for MIL-L-7808) all the Mg reacted with the MIL-L-23699 lubricant and a brown precipitate was produced. A light tan powder with B.P. > 250°C was isolated from the reaction mixture (Mg-I). The light tan powder was dissolved in a minimum amount of ethanol affording a brown solution and was reprecipitated with the addition of pentane. The precipitated solid, Mg-II, was white and contained 50.1%C, 8.65%H, and 10.8% Mg, and no P or N. The analytical data affords an empirical formula of $(\text{Mg C}_{10} \text{H}_{20} \text{O}_4)_x$.

The remaining brown solution was evaporated to produce a brown solid, Mg-III, which contained 56.3%C, 8.95%H and 9.0% Mg and no P or N. Therefore, the empirical formula for Mg-III is $(\text{Mg C}_{13} \text{H}_{26} \text{O}_4)_x$.

The infrared spectra of Mg-II and Mg-III are shown in Figure 25 and 26. Both spectra contain a strong broad band centered around 1575 cm^{-1} which is indicative of a metal carboxylate but the spectrum of Mg-III also contains a peak at 1740 cm^{-1} which is indicative of a carbonyl group. The H^1 NMR spectrum of the unreacted oil, except for the peak assigned to the pentaerythritol protons at 5.2 τ , is almost indistinguishable from the NMR of Mg-I. This observation also indicates the formation of Mg carboxylates.

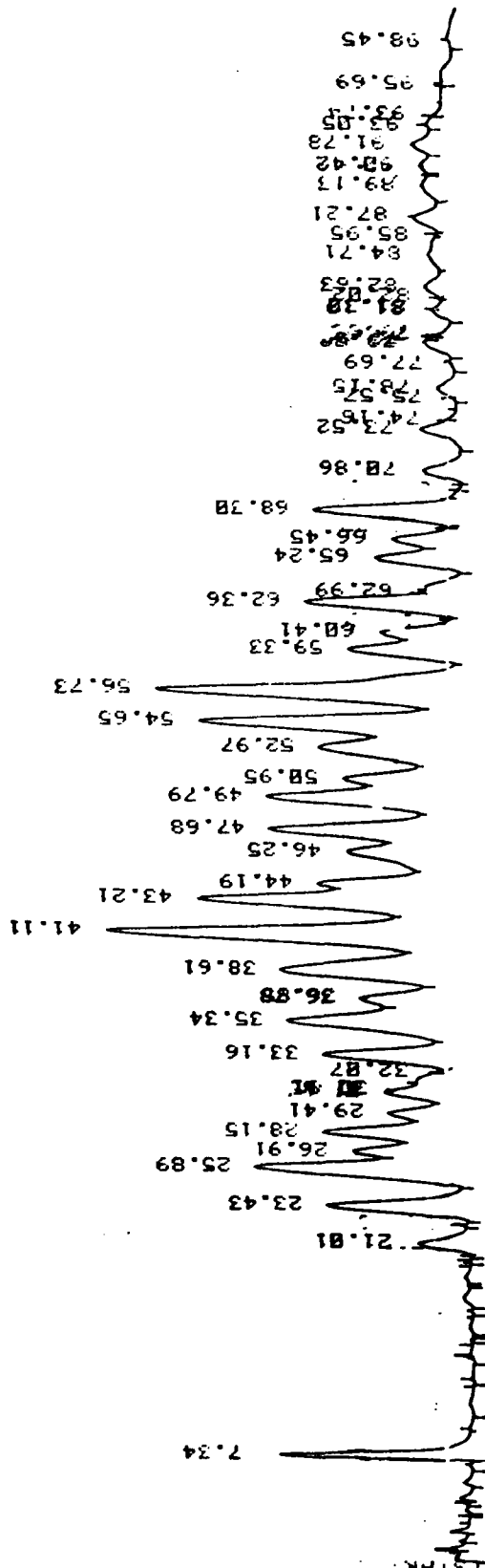


Figure 22. Gas Chromatogram of Mobil MIL-L-23699.

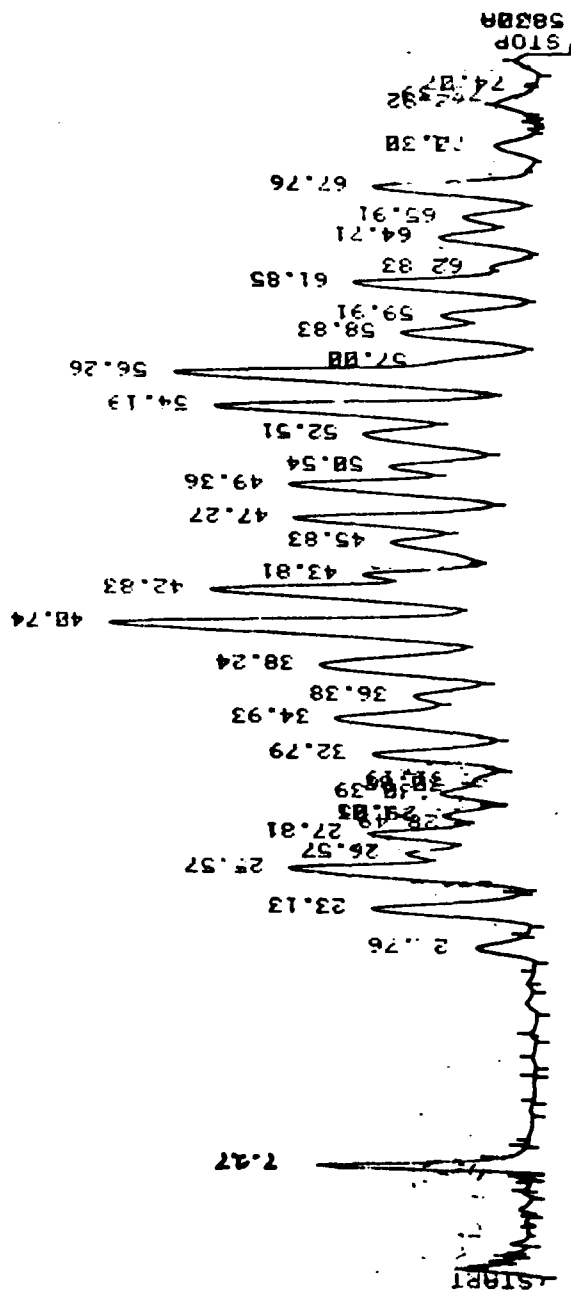


Figure 23. Gas Chromatogram of Mobil MIL-L-23699 After Heating at 240°C for 8 Hours.

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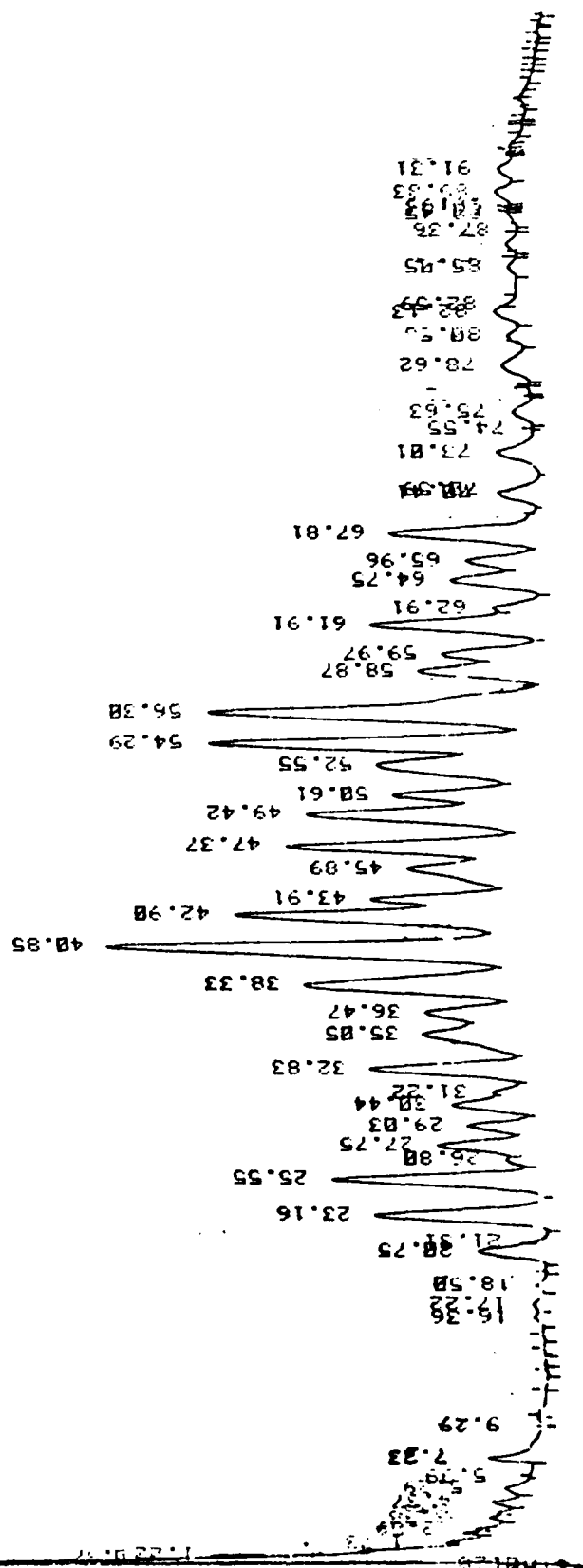


Figure 24. Gas Chromatogram of Mobil MIL-L-23699 After Heating at 240°C for 8 Hours in the Presence of Mg.

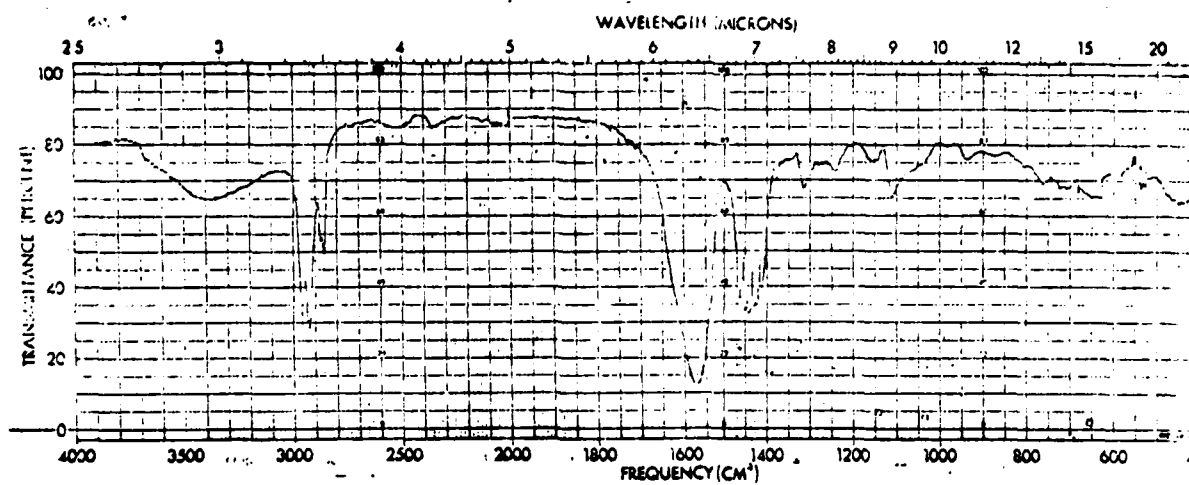


Figure 25. Infrared Spectrum of $(\text{Mg C}_{10} \text{H}_{20} \text{O}_4)_x$.

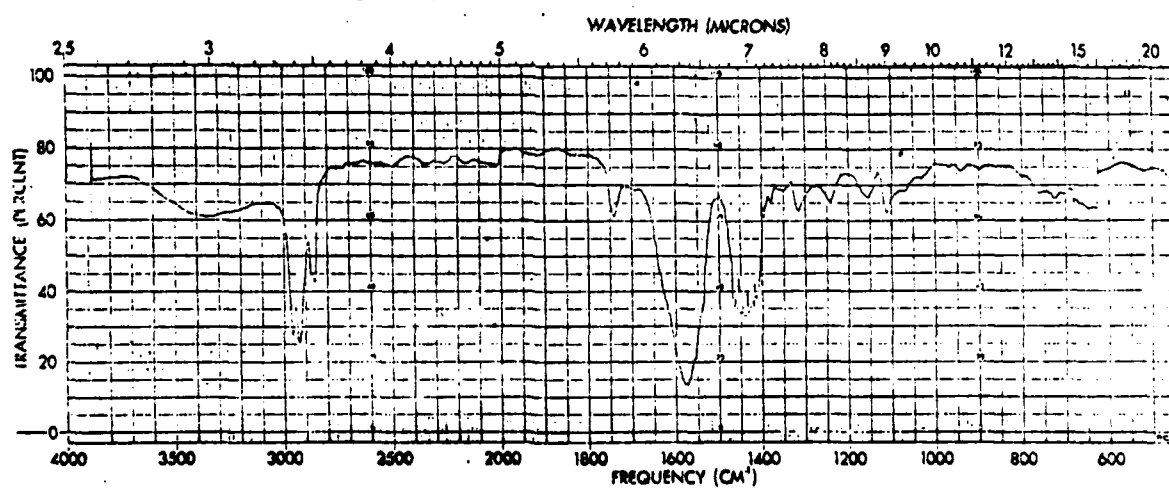


Figure 26. Infrared Spectrum of $\text{Mg (C}_{13} \text{H}_{26} \text{O}_4)_x$.

From all the evidence obtained on Mg-II and Mg-III it is concluded that they are formed from the reaction of Mg with carboxylic acids produced by the decomposition of the esters. The phosphate ester or antioxidant additives do not participate in the reaction as they do in the case of the reaction between MIL-L-7808H and Mg. Also the organometallic compound formed during the reaction of MIL-L-23699 oil and Mg has a limited solubility unlike the soluble Mg product formed with MIL-L-7808H oil.

3. IDENTIFICATION OF WEAR DEBRIS

a. Development of Analytical Methods

(1) Introduction

The second stage of the investigation was directed toward the development of a procedure which could differentiate among free metal (due to mechanical wear), metal oxide (due to oxidative corrosion), and organometallic species (due to chemical corrosion) in used ester lubricating oils. This procedure is required since spectroscopy can only determine the total metal content in used lubricating oil and not the chemical nature of the metal species. The organometallic compounds produced by the high temperature reaction of the metal or metal oxide powders with oil (Section I) were used to develop the procedures. Filtrations through 0.6 μ m Nuclepore membrane filters were incorporated into the method to separate dissolved (passed thru 0.6 μ m) from undissolved metal species.

(2) Experimental

(a) Dissolved Organometallic Degradation Products

The dissolved organometallic species of Zn, Cu, Mg and Fe used in this section were the reaction products isolated from the high temperature reactions of the metal powder and the lubricant. Each solution was diluted with the appropriate amount of Mobil MIL-L-7808H or 23699 to produce approximately 100 ppm solutions. The 100 ppm solutions were combined in equal

parts to produce a solution for Mobil MIL-L-7808H that contained 25 ppm of Zn, Cu, Mg and Fe and for Mobil MIL-L-23699 that contained 50 ppm of Mg and Fe. Analysis of the MIL-L-7808 solution revealed that the concentrations were 25, 30, 30 and 25 for Fe, Cu, Mg and Zn, respectively.

(b) Dissolved Metal Standards

Single element (500 ppm) dissolved metal standards were prepared by dissolving 50.0 ± 0.2 mg of Mg, Fe, Cu or Zn metal powder (ROC/RIC) in a minimum amount of aqua regia and diluting to 100 g with distilled H_2O . Single element standards containing 100 and 50 ppm were prepared by diluting the 500 ppm standards with the appropriate amount of distilled H_2O . Distilled H_2O was used as the blank.

(c) Standards for Extractions

The single element (500 ppm) dissolved metal standards were diluted to 100 and 50 ppm with the appropriate amount of distilled H_2O /solvent solution. The solvents used were methanol, ethanol, isopropanol, acetone, pyridine, piperidine or dimethyl sulfoxide. The ratio of distilled water to solvent was equal to the ratio used during extraction. Blanks were prepared in the same manner as the standards.

(d) Extraction Procedures

Filtering

The dissolved and particulate Mg, Fe, and Cu species were separated by filtering using the following procedure:

1. Oil sample is agitated.
2. Five to six 2-g aliquots are weighed out.
3. Each aliquot is diluted with 5 g pentane.
4. Each aliquot is filtered through a $0.6 \mu m$ filter.
5. Each filter is washed with 5 g pentane.

6. Filtrates are all combined.
7. Pentane is allowed to evaporate overnight.
8. Filtrate is placed under vacuum to remove residual pentane.
9. Filters are placed under vacuum to remove residual pentane.

Upon completion of the above procedure, one should have 10-12 g filtrate and 5-6 filters depending on the number of aliquots filtered.

Analysis of Filtrate

A 2-g aliquot of the filtrate was diluted 1:4 with MIBK and analyzed for Cu, Fe and Mg using the SMI-III. The results will determine the total concentration of Mg, Fe and Cu in the filtrate.

If Fe was detected in the filtrate, one more 2-g aliquot of the filtrate was weighed into a 1-oz polyethylene bottle. Ten grams of piperidine was added and the resulting solution was ultrasonically agitated for 30 min at 55°C. After 30 min each solution was further diluted with 2 g of distilled water and 2 g of pentane, shaken by hand and then centrifuged for 1 min during which time two layers formed. The top layer was oil/pentane and the bottom layer was piperidine/H₂O. Six grams of the bottom layer was pipetted for spectrometric Fe analysis. The analytical result is indicative of the concentration of organometallic Fe in the filtrate.

If Mg was detected in the filtrate, a 2-g aliquot of the filtrate was weighed into a 2-oz polyethylene bottle. Eight grams of the 50/50 ethanol/isopropanol solution was added and the resulting solution shaken at room temperature for 30 min on the paint shaker. After shaking, 2 g of distilled water is added and the resulting mixture thoroughly shaken by hand. The solution was centrifuged for 1 min during which time two layers separated with ethanol/isopropanol/water on top and oil on the bottom. Six grams of the top layer was pipetted

and analyzed for Mg. The analytical result is indicative of the concentration of organometallic Mg in the filtrate.

If Cu was detected in the filtrate, two 2-g aliquots of the filtrate were weighed out. One aliquot was diluted with 8 g of piperidine and the other aliquot was extracted with 8 g of distilled water. The resulting piperidine solutions were ultrasonically mixed for 30 min at 55°C and the resulting H₂O/oil mixtures were shaken for 30 min on the paint shaker. After 30 min each solution was further diluted with 2 g of pentane, shaken by hand, and then centrifuged for 1 min during which time two layers separated. The top layer was oil/pentane and the bottom layer was either piperidine/H₂O or H₂O depending on which solvent was used for the extraction. Six grams of the bottom layer was pipetted for spectrometric Cu analysis. Water extracts only organometallic Cu species while the piperidine extracts both metallic Cu and organometallic Cu.

Analysis of Filters

One of the filters was used to determine the total metal collected. The filter was placed into a 2-oz bottle and 4 g of aqua regia was added. The filter and acid were ultrasonically agitated for 20 min at 55°C to dissolve any metallic residue collected on the filter. The acid was then diluted with 16 g water and analyzed on the SMI for total Mg, Fe and Cu content.

If Fe was detected on the filter, another filter was treated with 8 g of piperidine and ultrasonically agitated for 30 min at 55°C. The resulting solution (the filter being completely soluble in piperidine) is diluted to 12 g with distilled water and centrifuged for 2 minutes. A 6-g aliquot of the solution was spectrometrically analyzed for Fe.

To determine the amount of organometallic Mg collected on the filter, one of the filters was treated with 8 g of ethanol/isopropanol and shaken for 30 min. After shaking, the solution was diluted with 2 g water and centrifuged for 2 min.

A 6-g aliquot of the solution was spectrometrically analyzed for Mg.

Two filters were used to analyze for Cu. One filter was treated with 8 g of piperidine solution and the other with 8 g of distilled water. Both solutions were ultrasonically agitated for 30 min at 55°C, then diluted with distilled water to give 10 g of each solution. The concentration of organo-metallic Cu particles was determined by analyzing the water extract. The concentraion of Cu determined in the piperidine extract results from the metallic Cu as well as organometallic Cu.

(3) Results and Discussion

The MIL-L-7808H oil solution containing 25, 30, 30, 25, ppm of organometallic Fe, Cu, Mg and Zn respectively was extracted with various reagent grade solvents including acetone, methanol, distilled H₂O, dimethyl sulfoxide (DMSO), isopropanol (IPA), pyridine, and piperidine. The results are listed in Table 52.

As seen in Table 52, all of the solvents are capable of partially or completely extracting organometallic Cu, Mg and Zn species from lubricating oils. However, none of the solvents were successful in extracting organometallic Fe at room temperature. At 55°C piperidine or pyridine was capable of quantitatively extracting organometallic Fe.

The same solvents were then tried on Cu, Mg, Fe and Zn metal powder (50 ppm each metal) and CuO, MgO and Fe₂O₃ oxide powder (80 ppm of each oxide) suspensions. The results listed in Tables 53 and 54 show that a 50/50 ethanol/isopropanol mixture does not extract the free metal or MgO. Therefore, this solvent was used to extract Mg organometallic species. Piperidine (dried over Na₂SO₄) at 55°C extracts organometallic Cu and Fe, free metallic Cu and MgO. Since piperidine extracts both organometallic Cu and free metallic Cu,

TABLE 52
EXTRACTION OF ORGANOMETALLIC
SPECIES DISSOLVED IN MIL-L-7808H OIL

<u>Solvent</u>	Metal Concentration Extracted (ppm)			
	<u>Cu</u>	<u>Mg</u>	<u>Fe</u>	<u>Zn</u>
H ₂ O	22.8	33.1	ND ^a	24.8
Methanol	27.0	28.5	ND	8.0
Isopropanol	19.3	24.5	ND	5.0
50/50 Ethanol/IPA	31.9	29.0	ND	- ^b
50/50 Ethanol/IPA ^c	-	48.0	ND	-
Acetone	20.8	8.7	ND	ND
DMSO	21.1	23.2	0.4	18.5
Pyridine	37.5	33.1	0.5	12.2
5% MeOH/Pyridine	26.0	27.0	ND	10.5
Piperidine (R.T.)	41.0	29.0	1.0	10.9
Piperidine (55°C)	31.9	ND	24.7	ND

a ND = not detected

b - = not analyzed

c in MIL-L-23699

TABLE 53
EXTRACTION OF METAL
POWDERS SUSPENDED IN MIL-L-7808H OIL

<u>Solvent</u>	Metal Concentration Extracted (ppm)			
	<u>Cu</u>	<u>Mg</u>	<u>Fe</u>	<u>Zn</u>
H ₂ O	ND ^a	10.0	ND	ND
Methanol	ND	20.0	ND	ND
Isopropanol	ND	ND	ND	ND
50/50 Ethanol/IPA	ND	ND	ND	ND
Acetone	7.2	ND	ND	ND
DMSO	15.0	ND	ND	ND
Pyridine	62.8	3.0	ND	3.8
5% MeOH/Pyridine	46.9	0.2	ND	ND
Piperidine (R.T.)	60.0	4.0	ND	2.0
Piperidine (55°C)	49.2	ND	ND	ND

Concentration of each Metal = 50 ppm

a ND = not detected

TABLE 54
EXTRACTION OF METAL
OXIDES SUSPENDED IN MIL-L-7808H OIL

<u>Solvent</u>	Metal Concentration Extracted (ppm)		
	<u>CuO</u>	<u>MgO</u>	<u>Fe₂O₃</u>
H ₂ O	ND	ND ^a	ND
Methanol	ND	ND	ND
Isopropanol	ND	ND	ND
50/50 Ethanol/IPA	ND	ND	ND
Acetone	4.5	ND	ND
DMSO	5.0	ND	ND
Pyridine	2.1	13.0	ND
5% MeOH/Pyridine	ND	9.3	ND
Piperidine (R.T.)	1.1	10.1	ND
Piperidine (55°C)	.7	29.0	ND

Concentration of each Metal = 80 ppm

^aND = not detected

a solvent which extracts only organometallic Cu was needed.

Distilled water, methanol, or IPA extracts only organometallic Cu and can be used in conjunction with the piperidine to differentiate between free metal and organometallic Cu.

Distilled H₂O or dimethyl sulfoxide (DMSO) can be used to differentiate organometallic Zn from free metal. Further work was not carried out on Zn since only 2 turbine engine lubricating samples out of 200 contained any appreciable Zn content.

b. Chemical Nature of Wear Debris in Used Lubricating Oils

(1) Introduction

In the final stage of this investigation the chemical nature of Fe, Mg and Cu wear debris in used lubricating oils was determined by employing the methods developed in the previous section, Ferrography and scanning electron microscope/energy dispersive x-ray analysis (SEM/EDAX). Used oil samples from the four categories, Failure (F), Hit (H), High PPM (P) and Routine (R), were examined to determine the effect the degree and amount of wear had on the chemical nature of the wear debris. Also used oil samples from different engines were examined to determine what affect the engine and oil type had on the chemical nature of the wear debris.

(2) Experimental

(a) ADM Procedure

Each used oil sample to be analyzed was shaken and a 2 g aliquot taken. Each aliquot was reacted with 0.4 g of the 1:8:1 (HF: HCl: HNO₃) acid mixture at room temperature and shaken on a vortex mixer for 5 minutes. The reaction mixture was then diluted with 9.6 g of the NeoCol/MIBK solvent and shaken until a clear solution formed. The diluted samples were then analyzed using the SMI-III to determine the metal content.

(b) Ferrography Procedure

Seven oil samples, were sent to AFWAL/POSL for Ferrographic analysis. The samples were heated to 65°C and agitated for 5 minutes. Three ml of the well agitated sample along with 1 ml of diluent were pumped across the slide. Fixer was then allowed to flow over the slide for ten minutes. The slides were viewed optically at 700X and pictures were taken of entry deposits at 280X. Percent area covered values were determined microscopically using an incident light densitometer. From this data the wear situation was rated as very low, normal, caution, or red alert.

The unused and Ferrographed (1:3 diluent: oil) portions were then analyzed for metal content. Three 1 g aliquots of the unused portion were individually diluted with 5 g of pentane and filtered through 0.6 µm Nuclepore membrane filters. The filters were then washed with an additional 5 g of pentane. The three filtrates and their pentane washings were combined. The pentane was removed by evaporation overnight followed by three hours under vacuum at 30°C. The three gram filtrate and a three gram aliquot of the unused oil sample were each diluted with 1 g of the Ferrographic diluent (obtained from AFWAL/POSL). A 2 g aliquot was taken of the diluted filtrate, the diluted unused oil, and the Ferrographed samples. Each 2 g aliquot was reacted with 0.4 g of the 1:8:1 acid mixture at room temperature and shaken on a vortex mixer for 5 minutes. Each reacted sample was then diluted with 9.6 g of the Neodol/MIBK solvent and shaken until a clear solution was formed. The diluted samples were then analyzed using the SMI-III to determine metal content.

(c) SEM/EDAX Procedure

The scanning electron microscope/energy dispersive x-ray analyses (SEM/EDAX) were performed on particulate matter on Nuclepore filters. Samples were cut from

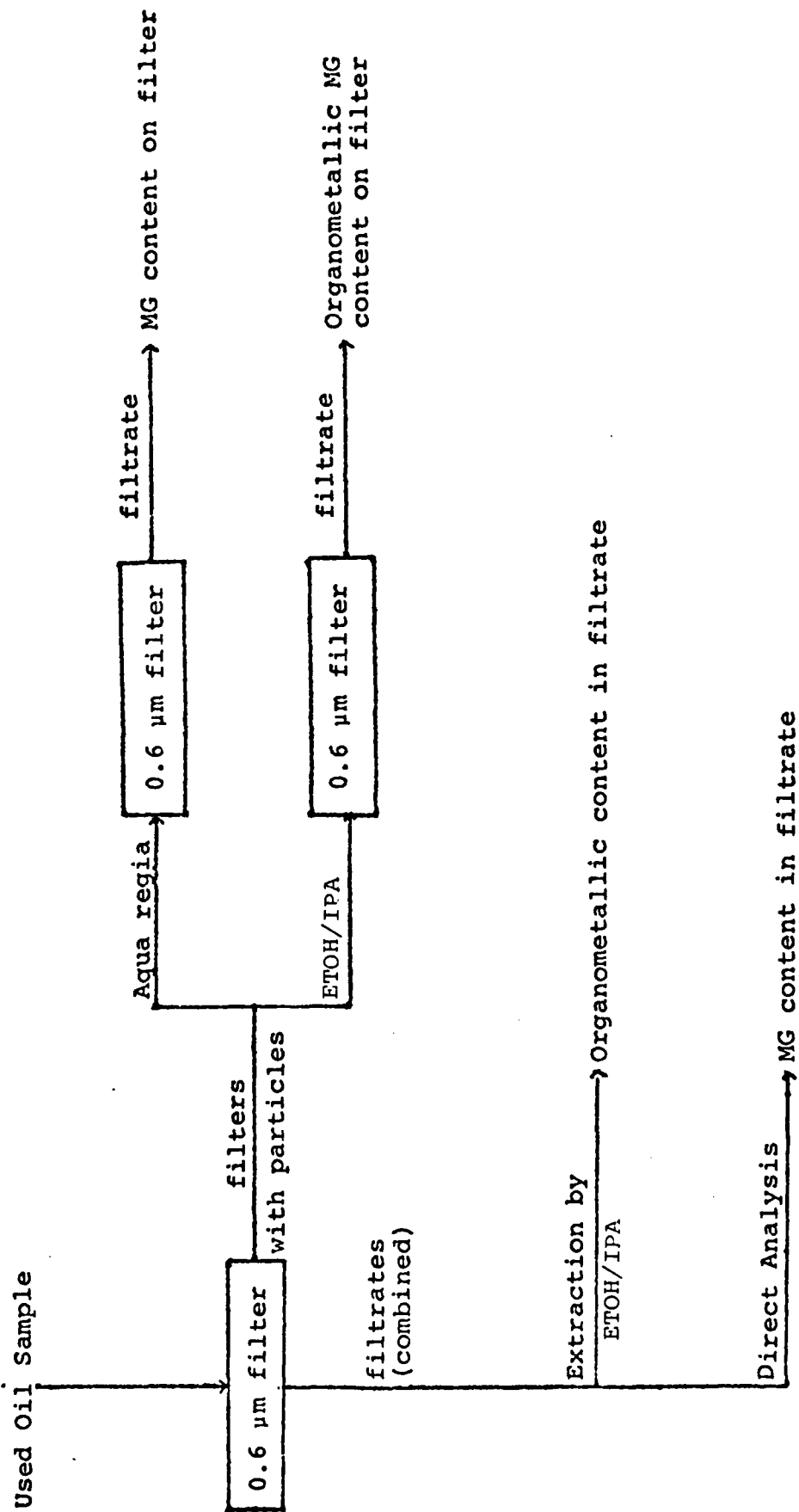


Figure 27. Flow Diagram for Extracting Mg From Used Oils.

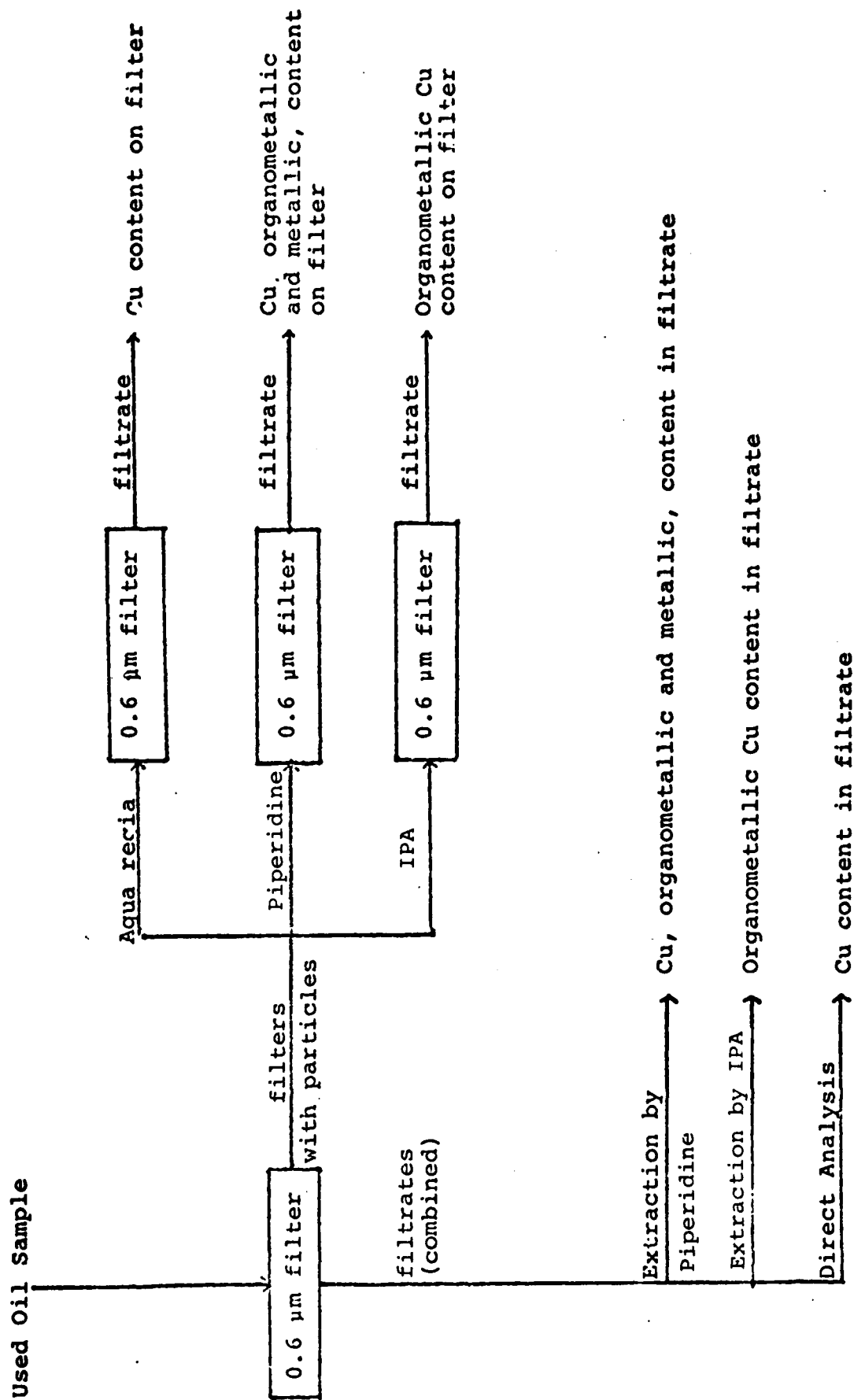


Figure 28. Flow Diagram for Extracting Cu From Used Oils.

Used Oil Sample

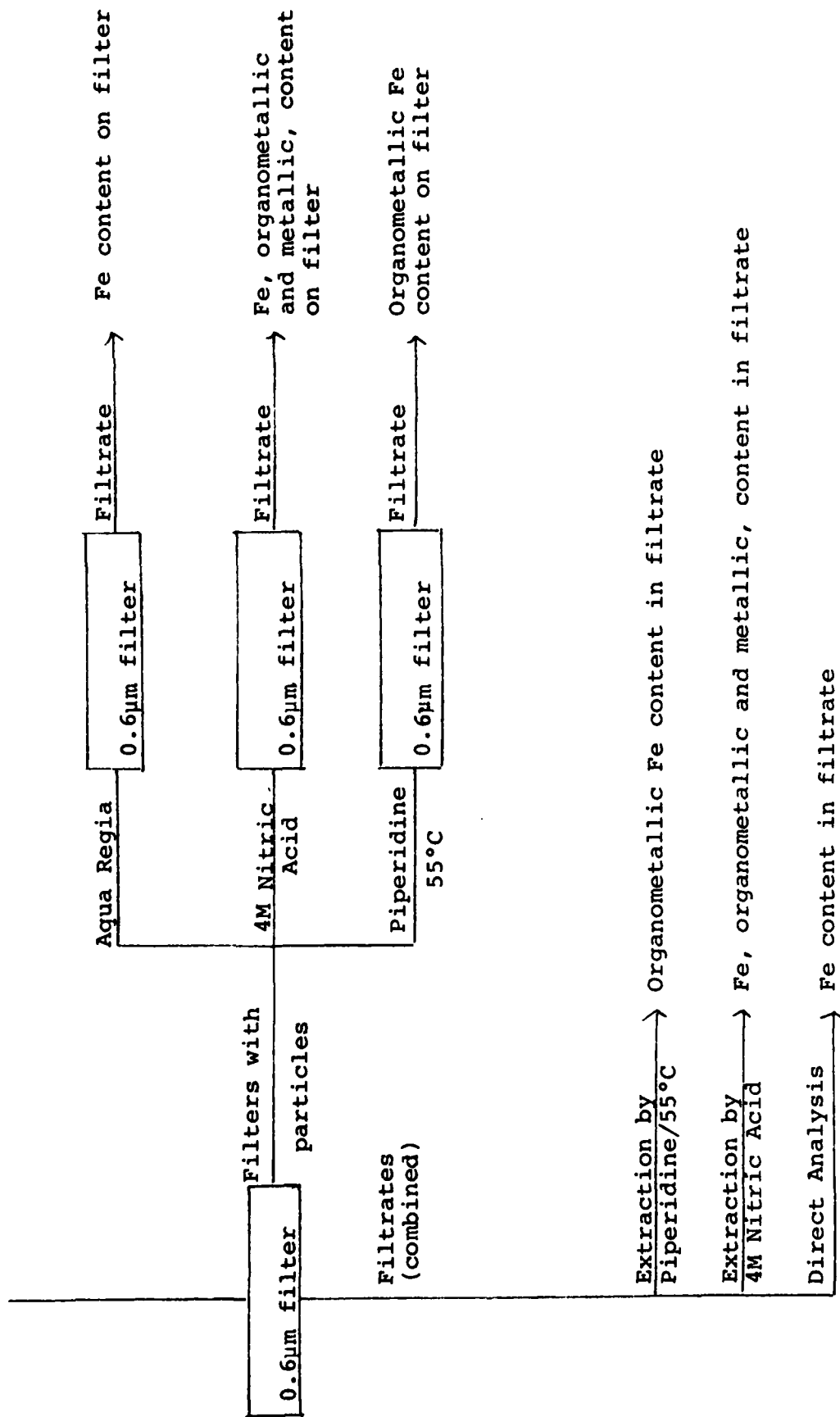


Figure 29. Flow Diagram for Extracting Fe From Used Oils.

the filter, mounted on a carbon specimen carrier, and coated with a thin layer of Au/Pd alloy for conduction purposes.

(d) Extraction Procedures for Fe, Cu, and Mg

The procedures used in this section are outlined in Figure 27, 28, 29.

(e) Calibration Standards for the ADM

The calibration standards were prepared from a D20-900 ppm Conostan metallo-organic alkyl aryl sulfonate concentrate. The 50 ppm standard was prepared by combining 0.5 g of the D20-900 ppm concentrate, 8.5 g Mobil MIL-L-7808 ester oil, 1.8 g of 1:8:1 acid, and 43.2 g of the Neodol/MIBK solution in a 4-oz polyethylene bottle and mixing thoroughly. The blank was prepared by combining 10 g of Mobil MIL-L-7808H ester oil, 2.0 g of 1:8:1 acid, and 48.0 g of Neodol/MIBK solution in a 4-oz polyethylene bottle and mixing thoroughly.

(f) Calibration Standards for Analysis of Ferrography Samples

The calibration standards were prepared from a D20-900 ppm Conostan metallo-organic alkyl aryl sulfonate concentrate. The 50 ppm standard was prepared by combining 0.37 g of the D20-900 ppm concentrate, 6.375 g Mobil MIL-L-7808H ester oil, 1.8 g of 1:8:1 acid, 2.250 g of Ferrographic diluting solution and 43.2 g of the Neodol/MIBK solution in a 4-oz polyethylene bottle and mixing thoroughly.

(3) Results and Discussion

(a) Determination of the Chemical Nature of Wear Debris by Extraction Procedures

The chemical nature of Mg wear debris was investigated first. The samples were divided into two groups according to the type of engine, T56 and non T56. This was done since 90% of the oil samples containing > 4 ppm Mg are from T56 engines. As seen in Table 55 the Mg present in every

TABLE 55
ANALYSIS OF USED OIL SAMPLES FOR Mg AND Fe

Sample No.	Engine	Total Mg (ppm)	Organometallic Mg (ppm)	% Mg Organometallic	Total Fe (ppm)	% Fe <0.6 μ m
F-14	T56	3.7	3.8	103	3.4	100
F-5	T56	6.3	6.2	98	12.4	94
F-19	T56	7.4	7.2	97	14.8	50
F-15	T56	7.6	7.6	100	61.5	53
F-28	T56	8.8	9.0	102	7.4	100
F-24	T56	9.6	9.9	103	4.1	100
F-39	T56	10.4	10.1	97	36.5	34
F-8	T56	11.4	11.2	98	6.7	73
F-37	TF39	5.8	5.6	97	7.6	46
H-14	T56	7.0	6.9	99	6.5	87
H-50	T56	10.1	9.8	97	3.7	98
H-6	T56	10.6	10.5	99	7.1	100
H-57	T56	12.8	12.6	98	4.7	83
H-68	T56	15.3	15.6	102	7.7	88
H-61	T56	16.9	17.0	101	12.3	97
H-43	T56	16.2	16.0	99	6.9	72
H-41	T56	18.3	17.9	98	22.2	44
H-47*	J79	8.4	3.0	68	12.6	24
H-54	J57	7.0	6.8	97	9.2	98
H-33	J50	8.9	8.8	99	3.6	102
P-5	T56	7.0	6.8	97	5.2	100
P-83	T56	25.3	24.8	98	17.9	97
P-106	T56	33.1	32.8	99	28.0	102
P-48	T56	37.2	37.8	102	14.2	98
P-61	T56	43.8	43.4	99	16.7	96
P-7	J79	3.2	3.3	103	5.6	100
P-1	J60	11.6	11.8	102	13.5	95
P-97	F100	29.6	30.1	102	28.0	99
P-58**	R2800	7.7	7.6	99	57.4	33
P-50**	R2800	2.2	2.1	96	45.9	18

TABLE 55
ANALYSIS OF USED OIL SAMPLES FOR Mg AND Fe (CONTINUED)

Sample No.	Engine	Total Mg (ppm)	Organometallic Mg (ppm)	% Mg Organometallic	Total Fe (ppm)	% Fe <0.6µm
R-107	T56	3.4	3.3	97	8.1	99
R-302	T56	4.3	4.3	100	3.3	98
R-5	T56	8.0	8.1	101	7.2	102
R-52	T56	8.5	8.6	101	4.8	97
R-3	T56	12.5	12.4	99	4.5	98
R-445	J69	3.8	3.7	97	4.1	97
R-424	J57	6.1	6.0	98	9.6	101

* Phosphorous additive depleted

** Hydrocarbon Oils

T56 oil samples is > 97% soluble organometallic regardless of the degree of mechanical wear (Fe particles > 0.6 μm). Therefore, in T56 engines the Mg wear debris is produced by chemical corrosion of component surfaces followed by dissolution into the surrounding fluid.

The Mg present in the non T56 oil samples (Table 55 is also > 97% soluble organometallic regardless of engine oil or degree of mechanical wear, except for H-47. In H-47 the Mg present is 36% soluble, organometallic; 42% organometallic particles (> 0.6 μm), and 28% metallic particles (> 0.6 μm). Unlike the other ester base non T56 samples, which contain 800-1700 ppm P, H-47 contains less than 20 ppm P. Therefore, the phosphate ester additive appears to increase the solubility of the organometallic species as predicted by the results obtained from the MIL-L-7808H and ester base stock reaction with Mg powder. Therefore, the Mg wear debris in the non T56 oil samples results from chemical corrosion similar to that for the T56 engine.

Therefore, since the Mg is present as a dissolved, organometallic species its concentration in used lubricating oils is accurately determined by the spectrometers used in the Joint Oil Analysis Program (JOAP).

The next metal investigated was Cu. Cu is present as organometallic, metallic and oxide species (Tables 56-59). Except for a few Hits (H47, 48 and 49) the organometallic Cu present is < 0.6 μm . The % Cu which is organometallic ranges from 26-80% for the T56 engine and 2-32% for the non T56 engines. The remaining Cu wear debris is basically metallic particles < 0.6 μm for the Routine and High PPM samples and ranges from < 0.6 μm up to \approx 50 μm in the Hit and Failure samples. The oxide particles present in the Routine and High PPM samples are < 0.6 μm and in the Failure and Hit samples range from < 0.6 μm to 50 μm . Whether the oxide particles are produced by mechanical wear of an oxide film

TABLE 56
ANALYSIS OF FAILURE SAMPLES FOR COPPER

Sample	Engine	Organometallic PPM	% Total	Oxide >0.6µm	<0.6µm	% Total	Metallic >0.6µm	% Total	Total Cu
F-22	T56	1.0	43	-	-	-	-	57	2.3
F-19	T56	3.0	53	0.7	0.7	12	-	35	5.7
F-26	J79	0.8	14	0.9	0.9	15	-	71	5.8
F-45	J79	1.0	16	0.7	0.7	11	0.5	73	6.3
F-37	TF39	0.5	7	2.5	2.5	53	0.9	40	6.6
F-39	T56	3.3	49	0.9	0.9	14	-	37	6.7
F-18	T56	6.4	38	1.8	1.8	11	-	51	17.0

TABLE 57
ANALYSIS OF HIGH PPM SAMPLES FOR COPPER

<u>Sample</u>	<u>Engine</u>	<u>Organometallic</u>		<u>Oxide</u>		<u>Metallurgical</u>		<u>Total</u>	
		<u>PPM</u>	<u>% Total</u>	<u><0.6µm</u>	<u>>0.6µm</u>	<u><0.6µm</u>	<u>>0.6µm</u>	<u>% Total</u>	<u>Cu</u>
P-5	T56	1.1	46	0.2	-	1.1	-	46	2.4
P-14	J69	1.6	32	0.4	-	3.0	-	60	5.0
P-35	J79	1.1	15	2.0	-	4.3	-	58	7.4
P-73	J79	1.1	16	2.7	-	3.2	-	46	7.0
P-83	T56	2.2	26	2.3	-	4.0	-	47	8.5
P-50	R2800	0.7	6	3.9	-	6.3	-	58	10.9
P-8	J79	1.4	12	1.5	-	9.1	-	75	12.0

TABLE 58
ANALYSIS OF HIT SAMPLES FOR COPPER

Sample	Engine	Organometallic		Oxide		% Total		<0.6µm		Metallic		% Total		Total
		PPM	% Total	<0.6µm	>0.6µm	% Total		<0.6µm		>0.6µm		% Total	Cu	
H-6	T56	3.1	53	2.2	-	38		0.5	-	-		9	5.8	
H-20	J85	1.1	16	2.3	-	33		3.6	-	-		51	7.0	
H-23	J79	1.3	13	4.2	-	42		4.5	-	-		45	10.0	
H-12	J79	1.8	17	1.2	-	11		7.5	-	-		72	10.5	
H-47	J79	0.7 ^a 1.4 ^b	20	1.4	-	13		4.0	3.2			67	10.7	
H-1	J79	1.2	7	0.4	-	2		6.0	9.0			91	16.6	
H-49	J85	0.6 ^a 3.3 ^b	17	2.7	3.7	28		6.6	6.1			55	23.0	
H-48	J85	9.2 ^a 7.1 ^b	2	71	108	27		60	405			71	660	

^a passed through 0.6 µm filter

^b retained on 0.6 µm filter

TABLE 59
ANALYSIS OF ROUTINE SAMPLES FOR COPPER

Sample	Engine	Organometallic PPM	% Total	Oxide PPM	% Total	Metallic PPM	% Total	Total Cu
R-79	J69	0.3	8	2.0	50	1.7	42	4.0
R-52	T56	3.6	80	-	-	0.9	20	4.5
R-71	T56	3.6	72	0.6	12	0.8	16	5.0
R-81	J79	0.8	13	1.6	27	3.6	60	6.0

formed on the component surface or through oxidation of the generated metallic particles cannot be determined by this method.

Since the Cu present is organometallic, metallic, and oxide in nature and ranges from $< 0.6 \mu\text{m}$ to $\sim 50 \mu\text{m}$ in size the Cu concentrations determined by OAP are not as accurate as those of Mg due to the particle size dependence of the spectrometer and the use of organometallic standards for calibration. The reliability of the Cu determination is still very high since the percentage of Cu particles $> 3 \mu\text{m}$ in any one sample is very low. Also, the absorption or emission instrumental conditions are almost identical for organometallic standards and particles less than $3 \mu\text{m}$ so that equal concentrations of standard and sample give equal readings.

The final and most important metal investigated was Fe. As can be seen in Tables 60-63 the Fe present is organometallic, metallic, and oxide in chemical nature. Unlike Cu, the percent of each chemical form for Fe is related to the degree of wear occurring. In every Failure and almost every Hit sample the Fe present is either $> 50\%$ organometallic or metallic, but in every High PPM and Routine sample, except P-5 and R-52, the Fe present is $> 50\%$ oxide. Again, as with Cu, whether the oxide is produced by mechanical wear of an Fe oxide film formed on component surfaces or oxidation of metallic particles cannot be determined by this method. Therefore, organometallic species (dissolved and particles) produced by chemical corrosion and metallic particles produced by mechanical wear make up the majority of the Fe wear debris found in lubricant samples from abnormally wearing engines. These findings are in full agreement with the data produced by Klaus⁽²⁷⁾ at various loads with a Shell four ball wear tester.

For the High PPM and Routine samples the OAP program is very accurate since all the Fe present is $< 0.6 \mu\text{m}$

TABLE 60
ANALYSIS OF FAILURE SAMPLES FOR IRON

Sample No	Engine	Organometallic			Oxide			Metallic			Total
		<0.6	>0.6	% Organo Total	<0.6	>0.6	% Oxide Total	<0.6	>0.6	% Metallic Total	
F-45	J79	1.2	-	35	-	-	-	2.2	-	65	3.4
F-8	T56	0.8	-	12	1.8	-	26	4.2	-	62	6.8
F-4	T56	3.6	-	42	1.3	-	15	3.6	-	43	8.5
F-33	J79	3.9	-	49	-	0.5	06	1.6	2.0	45	8.0
F-37	TF39	0.5	-	04	0.7	2.7	27	4.0	4.8	69	12.7
F-5	T56	4.1	-	34	-	-	-	8.0	-	66	12.1
F-19	T56	0.7	2.4	13	0.9	1.7	11	7.0	12.0	77	24.7
F-22	T56	8.4	1.2	38	1.0	0.5	06	7.6	6.5	56	25.2
F-39	T56	0.9	2.5	12	2.5	2.0	15	2.5	20.0	74	30.4
F-26	T56	5.3	15.5	48	6.2	10.0	38	1.7	4.5	14	43.2

TABLE 61
ANALYSIS OF HIT SAMPLES FOR IRON

Sample No	Engine	Organometallic			Oxide			Metallic			Total
		<0.6	>0.6	% Organo Total	<0.6	>0.6	% Oxide Total	<0.6	>0.6	% Metallic Total	
H-6	T56	1.8	-	22	-	-	-	6.4	-	78	8.2
H-1	J79	1.9	1.2	57	-	-	-	1.3	1.0	43	5.4
H-47	J79	1.2	3.1	30	3.6	2.8	44	2.8	0.9	26	14.4
H-4	TF30	4.3	-	35	-	-	-	8.0	-	65	12.3
H-14	T56	5.7	-	36	1.0	-	06	9.0	-	58	15.7
H-9	J75	7.5	-	36	2.5	-	12	11.0	-	52	21.0
H-18	J85	10.8	-	45	3.1	-	13	10.0	-	42	23.9
H-41	T56	1.9	2.1	16	2.4	4.0	25	5.2	10.0	59	25.6
H-49	J85	3.4	5.0	25	10.0	7.1	51	2.1	5.8	24	33.4
H-23	J79	2.8	14.8	23	5.0	24.0	38	13.1	15.7	39	75.4
H-48	J85	1.4	46.5	12	1.5	21.0	06	11.0	314	82	395.4

TABLE 62

ANALYSIS OF HIGH PPM SAMPLES FOR IRON

Sample	Engine	Organometallic		Oxide		Metallic		Total
		PPM	% Total	PPM	% Total	PPM	% Total	Fe
P-7	J79	0.3	5	4.3	75	1.1	19	5.7
P-5	T56	0.7	13	1.4	26	3.3	61	5.4
P-1	J60	3.2	25	8.7	68	0.9	7	12.8
P-48	T56	0.5	3	9.5	66	4.5	31	14.5
P-61	T56	0.3	2	8.5	53	7.2	45	16.0
P-83	T56	3.3	19	8.3	48	5.7	33	17.3
P-97	T56	2.4	9	17.9	64	7.7	28	28.0
P-106	T56	4.0	14	20.0	69	5.0	17	29.0
P-58	R2800	1.4 ^a	30	11.0 ^a	37	8.0 ^a	33	57.4
		16.0 ^b		10.0 ^b		11.0 ^b		

^apassed through 0.6 μ m filter^bretained on 0.6 μ m filter

TABLE 63
ANALYSIS OF ROUTINE SAMPLES FOR IRON

Sample	Engine	Organometallic		Oxide		Metallic		Total
		PPM	% Total	PPM	% Total	PPM	% Total	Fe
R-302	T56	0.4	12	2.5	76	0.4	12	3.3
R-445	T69	1.0	24	1.8	44	1.3	32	4.1
R-3	T56	0.2	4	3.7	82	0.6	13	4.5
R-52	T56	2.0	42	0.8	17	2.0	42	4.8
R-5	T56	0.6	8	5.2	72	1.4	19	7.2
R-107	T56	2.1	26	4.1	51	1.9	23	8.1
R-424	J57	0.8	8	6.3	66	2.5	26	9.6

in size. The accuracy of the spectrometers used in OAP is significantly lower for the Hit and Failure samples. In several samples the spectrometer is blind to > 50% of the Fe metal present, but in these samples the Fe detected by the spectrometer was high enough to have the engine inspected for abnormal wear.

(b) Examination of Wear Debris by SEM/EDAX

Examination of the samples in the scanning electron microscope showed that all filters were covered with numerous particles, some metallic, some organic and some geological in nature. The organic particles are characterized by the presence of light elements and the absence of metallic elements. The particles of geological origin are characterized by the presence of aluminum and silicon together, iron and titanium together, silicon (quartz), aluminum and calcium together, and silicon and calcium together. The metallic particles normally contain only common metallic elements such as iron, iron + chromium + nickel, copper + zinc, copper + nickel, aluminum and aluminum + silicon. Table 64 summarizes the results as reported by the UDRI SEM Lab for the 10 filtered samples studied. The limitation of the technique is that the detector is not sensitive to the elements lighter than sodium. Therefore, the presence of oxides could not be determined by this technique. Also dissolved species are not retained by the filters.

(c) Examination of Wear Debris by Ferrography

Five used oil samples were analyzed by AFWAL/ POSL on their Ferrograph. The Ferrographic data gathered on the other five samples is as follows:

R-4

Extremely large amount of ferrous and copper/ brass debris. Also, some white metal (Al or Mg). Rubbing wear

TABLE 64
ENERGY DISPERSIVE X-RAY ANALYSIS
OF FILTERED PARTICULATES

SAMPLE PID 1a	MAJOR ELEMENTS	# OF PARTICLES
	Si, Ca	1
	Si, Ti	1
	Fe, Cu	1
	Fe, Cr	6
	Fe	1
	Si	2
	Fe, Cr, Ni	1
	Si, Cl	1
	Organic or Light Elements	9
1u H-48 2g	Cu, Fe, Zn Fe, Cu, Cr	16 4
F17 1u	Fe S, Si, P Ag Zn Si, Ni Organic or Light Elements	4 2 3 1 3 8
H-49 4u	Cl	2
	Cu, Fe, Ni Cr, Fe, Cu S Fe Organic or Light Elements	1 1 1 1 19
H-48 9u	Fe, Cr Cu, Zn Fe, Cu	6 8 6
H-48 10u	Cu, Zn Fe, S Fe, Cu Organic or Light Elements	10 1 3 3
F-17 4u	Fe Al, Si Ag Organic or Light Elements	8 2 1 8
F-26 1u	Fe	3
Si, Fe	Si, Al, Ca Si Ca, Fe Al, Si Organic or Light Elements	2 7 1 1 2 7
P2	Cl, Ni Fe Fe, Ag Al, Fe S - light elements Si, Ca - light elements Organic or Light Elements	1 4 1 1 1 3 8
P4	Si, Fe Ca, Fe Fe Si Ca Si, Zn Al, Si Al S, Mo Organic or Light Elements	1 1 3 1 2 1 1 1 1 10

was primarily ferrous, while fatigue chunks were both ferrous and Al/Mg. The presence of fatigue and laminar wear suggest gear involvement. Minor amounts of cutting wear and oxides were found. Some ferrous debris was "blued" indicating higher than normal temperatures. Based on the Ferrographic data, the wear was rated as caution/very high.

H-18

The sample contained only moderate amounts of ferrous debris. Most of the ferrous debris was very small. Some oxides were also noted. However, the debris which caused a very high rating to be assigned was fatigue chunks of bright metal. The chunks are not magnetic. Upon heating they do not blue, but slightly tarnish. Also, particle edges are not torn as often found with Al/Mg type materials. The material may be a high alloy of Fe/Cr/Ni, based upon SOAP. The uniformity of particles suggest possibly only one source.

H-49

Huge amounts of debris. Rubbing wear, fatigue chunks, laminar, severe and cutting wear are present. Also, severe wear sections of copper/brass are abundant. Much of the ferrous wear is of low alloy type. This unit based upon Ferrography would be rated as a failure for any type of turbo-machine. A suggested failure mechanism is initial failure of bearing separator followed by rolling element loss. The order of failure, i.e., cage then element could be reversed.

H-56

The Ferrogram indicated that the wear situation was normal/caution. The amount of debris was not high. Only the presence of small amounts of spheres and cutting wear suggest some caution.

P-66

Wear situation rated as caution due to amounts

of small wear debris mixed with oxides. Ferrous debris appears to be of low alloy type. More ferrous debris is present than reported by SOAP at 1 ppm. Larger metallic particle types are not prominent. If oxides were not present, the severity rating would be reduced significantly. The presence of oxides may only indicate that an oil change is required.

As can be seen from the data many different types of mechanical wear; rubbing, fatigue, cutting, etc. are occurring in the same jet engine. Also both metallic and oxide wear particles were observed in most of the samples.

Seven more used oil samples were analyzed by AFWAL/POSL to determine the particle size limitation of the Ferrograph. The samples which passed through the Ferrograph and the original samples were returned to us and analyzed by the particle size independent method for wear metals. Also aliquots of the original samples were filtered through a 0.6 μm filter and the filtrates analyzed by the same procedure. The results of the metal analyses are listed in Table 65. All elements with concentrations greater than 1 ppm before being Ferrographed are listed. The ratings based on Ferrographic analyses and calculated efficiencies are also listed in Table 65.

As seen in Table 65 the concentration of the wear metal in the 0.6 μm filtrate and Ferrographed sample is equal in almost every sample. Therefore, the Ferrographic data is for wear debris > 0.6 μm in size and does not include metallic or oxide particles produced during normal mechanical wear or dissolved organometallic species produced by corrosion. The percentage of wear debris for each metal present in the oil sample deposited by the Ferrograph ranges from 0.0 to 68%. Therefore, the Ferrographic data is based on less than half of the wear debris present in each oil sample, but provides a valuable insight into the type of abnormal wear which is producing the large particles.

TABLE 65

METAL ANALYSES OF FERROGRAPHED OIL SAMPLES

Sample No.	Element	Metal Concentration (ppm)			% Efficiency**	Ferrographic Wear Rating
		A*	B*	C*		
R-19	Fe	7.2	5.8	5.8	19.4	Normal
	Pb	2.0	1.5	1.7	25.0	
H-31	Fe	19.3	15.7	16.0	18.7	Normal
	Cr	1.7	1.0	1.7	41.2	
	Ni	2.2	1.8	2.0	18.2	
H-44	Fe	15.9	5.1	5.8	67.9	Red Alert
	Cu	3.0	2.0	2.9	33.3	
P-4	Fe	10.9	8.3	9.1	23.8	Normal
P-21	Fe	14.6	12.9	13.1	11.6	Normal
F-26	Fe	49.3	19.3	20.1	60.9	Red Alert
	Al	3.2	1.5	1.6	53.1	
	Cr	3.5	1.8	2.0	48.6	
	Cu	7.4	3.6	3.9	51.4	
	Mg	1.9	1.5	1.4	21.1	
F-33	Fe	9.0	4.7	5.7	45.6	Caution
	Cu	1.3	1.4	1.4	00.0	
	Zn	3.0	1.2	1.2	60.0	

*A = Sample before Ferrographic analysis

B = Sample after Ferrographic analysis

C = 0.6 μ m filtrate of A

**% Efficiency = (A-B/A) 100

SECTION VI

DEVELOPMENT OF ATOMIC ABSORPTION PROCEDURES

1. INTRODUCTION

The need to maximize fleet readiness and equipment reliability has focused attention on the problems associated with detecting wear of oil wetted components. The detection of wear metal particulates is of critical importance since their presence is indicative of component wear and they often accelerate the complex wear mechanisms that degrade component surfaces.

The success of oil analysis lies in the assumption that wear metal concentrations are determined accurately and precisely. With proper care and skill the atomic absorption operator can easily analyze wear metals with the required accuracy and precision.

Atomic absorption spectrometry is an analytical method for the determination of elements based on the absorption of radiation by free atoms. When properly operated, atomic absorption spectrometry offers a number of advantages. The instrument is relatively inexpensive, and the technique is specific, has low limits of detection, and gives accurate and precise results for homogeneous samples. To fully utilize these capabilities, the instrument parameters should be optimized for the types of samples being analyzed. This section covers the research carried out to arrive at the optimum procedures for analyzing lubricating oils for wear metals by atomic absorption spectrometry.

The atomic absorption process occurs when ground state atoms absorb light of specific wavelengths which force ground state atoms into excited states. The amount of light absorbed is proportional to the number of ground state atoms in the light path. The relationship between the amount of light absorbed for the sample and the amount of light absorbed for standard solutions can be used to determine the element's concentration in the sample.

There are a few inherent difficulties in determining wear metal concentrations by atomic absorption spectrophotometry which are largely beyond the operators control. The first factor to consider is the efficiency of the sample introduction system which consists of a nebulizer, a spray chamber and a burner head. The efficiency of transporting wear metal particulates to the flame where they can be analyzed is inversely proportional to the size of the particle. Experiments have shown that wear metal particles larger than 10-15 μm are not effectively transported to the flame.

The temperature of the flame is also important and must be high enough to vaporize any metallic wear metal particles which are transported to the flame. Since the nitrous oxide-acetylene flame has a higher temperature than the air-acetylene flame, its use is recommended for the accurate determination of wear metals in used lubricating oils.

Another factor of importance is the particle's residence time in the flame before the absorption of light is measured. The analyte residence time is directly related to the observation height which is the distance from the top of the burner head to the center of the light beam emitted by the hollow cathode lamp. Obviously, larger observation heights require the analyte to remain in the flame longer before the absorption of light is measured.

As expected, large particles require a longer residence time (higher observation heights) in the flame before maximum absorption is observed. If standards could be prepared which contained particles of the appropriate sizes, the instrument could be optimized for the detection of wear metal particles. However, since it is very difficult to prepare standards with reproducible particles sizes, the recommended procedure is to optimize the flame conditions using Conostan standards which are provided by the JOAP Technical Support Center, NAS, Pensacola, FL.

Since Conostan standards are oil soluble metalloorganic, alkyl aryl sulfonates their use as calibration standards results in flame conditions which are not optimum for the analysis of particles larger than 1-3 μm . Although particles as large as 10-15 μm are being transported to the flame, they are not totally vaporized at the optimum observation heights determined using Conostan standards. Therefore, in addition to the direct analysis of used lubricants, a method is described which dissolves any metallic particles present in the lubricant and provides a homogeneous solution for AAS analysis. Since the solution is homogeneous, the wear metal can be quantitatively analyzed at observation heights and flame conditions identical to those determined with Conostan standards.

2. DEVELOPMENT OF PROCEDURES FOR THE DIRECT ANALYSIS OF USED LUBRICATING OILS

a. Introduction

The basic atomic absorption instrument requires a primary light source, such as a hollow cathode lamp, an atomizer, such as a flame, a monochromator to isolate a specific wavelength of light, and a detector with associated electronics to accurately measure the light signal and convert the signal into usable form. The optimum detection of wear metals occurs when the primary light source, the monochromator, and the detector are optically aligned, and the atomizer is producing the maximum number of ground state atoms.

This section describes the work carried out to arrive at the recommended procedures for the analysis of wear metals. Optimization of the procedures deals mainly with adjustments carried out to maximize the efficiency of the atomizer which is, in this case, the nitrous oxide-acetylene flame. Parameters such as wavelengths, dilution factors, gas flow rates and observation heights were investigated and optimized so that wear metal concentrations can be determined with the required accuracy and precision. The detection limits at the optimum conditions are also reported.

b. Wavelength Selection

The wavelengths selected (Table 66) for the analysis of wear metals is straightforward. The commonly used atomic absorption lines and their relative sensitivities are taken from the Perkin-Elmer methods book.⁽¹⁴⁾ The wavelengths recommended for wear metal determinations are usually the strongest and will provide the greatest sensitivity. The exceptions are Ni, Pb and Sn where the 341.5 nm, 283.3 nm and the 286.3 nm lines are recommended, respectively. The most sensitive Ni, Pb and Sn lines at 232.0 nm, 217.0 nm and 224.6 nm, respectively, appear in the wavelength region where appreciable background absorption occurs in the nitrous oxide-acetylene flame. The absorption of UV radiation by the flame makes determinations using wavelengths below 250 nm less precise.

The lines chosen for some of the elements are too sensitive for the analysis of samples containing high concentrations of wear metal. For example, with the dilution ratio recommended, the iron working curve determined at 248.3 nm is linear to only 50 ppm. To determine concentrations of iron greater than 50 ppm it is necessary to dilute the sample further so the measured absorption falls within the linear range or select another absorbing line of lower absorptivity. A useful alternative line for iron occurs at 372 nm and gives a working curve which is linear to at least 100 ppm.

Sensitivity is also effectively decreased by rotating the burner head about its vertical axis so that the light beam passes through a narrow section of the flame. Therefore, for the determination of Mg, the burner head should be rotated 90° about the vertical axis so that Mg can be determined using the recommended absorption lines at 285.2 nm.

c. Flame Optimization

The flame temperature is largely dependent on the choice of fuel and oxidant. The air-acetylene flame's temperature is approximately 2300°C while the nitrous oxide-acetylene flame's

TABLE 66
WAVELENGTHS USED FOR ATOMIC ABSORPTION
WEAR METAL ANALYSES

Element	Wavelength
Ag	328.1
Al	309.3
Cr	357.9
Cu	324.7
Fe	248.3
Mg	285.2
Mo	313.6
Ni	341.5
Pb	283.3
Si	251.6
Sn	286.3
Ti	365.4

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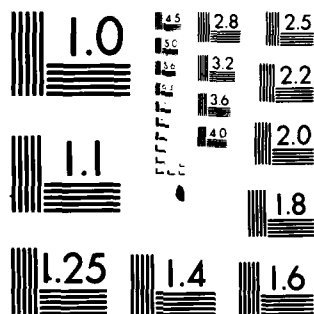
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MICROCOPY RESOLUTION TEST CHART
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temperature is approximately 2900°C. Because of its higher temperature, we recommend the nitrous-oxide acetylene flame for the analysis of wear metals. The higher temperature of the nitrous oxide-acetylene flame vaporizes the wear metal particles that reach the flame more efficiently than the air-acetylene flame and provides higher recoveries of wear metal particulates. The nitrous oxide-acetylene flame also minimizes chemical and interelement interferences. In addition, the nitrous oxide-acetylene flame is required for the accurate analysis of refractory elements such as Al, Si, Sn, Mo and Ti. Oil build up on the burner head is less likely to occur with the nitrous oxide-acetylene flame resulting in a stable flame and more accurate analyses.

In optimizing the flame conditions for each element, the fuel/oxidant ratio is adjusted to give flame conditions which maximize the population of ground state atoms. The optimized flow rates are given in Table 67 for each element. Elements such as Ag and Cu require a lean (oxidizing) flame while elements such as Si, Sn, Ti and Mo require a rich (reducing) flame for maximum sensitivity. The fuel rich flame does present the problem that carbon builds up on the burner head slot and needs frequent cleaning.

To achieve maximum sensitivity the measurements are made after adjusting all instrumental conditions to achieve maximum absorption. Therefore, measurements are obtained by observing the portion of the flame which contains the highest number of ground state atoms. The population of ground state atoms is expected to vary with respect to analyte residence times (observation height), fuel oxidant ratios and flame temperatures.

d. Observation Height

The effect of analyte residence time is related to observation height where the observation height is defined as the vertical distance between the light beam and the top of the

TABLE 67

OPTIMIZED FLOW RATES FOR WEAR METAL ANALYSES
USING THE NITROUS OXIDE-ACETYLENE FLAME

<u>Element</u>	<u>Fuel Flow Rate^b</u> <u>L/min</u>	<u>Type Flame</u>
Ag	2.4	lean (oxidizing)
Al	4.4	
Cr	4.4	
Cu	2.4	lean (oxidizing)
Fe	4.4	
Mg ^a	3.7	
Mo	5.2	rich (reducing)
Ni	4.8	
Pb	4.4	
Si	5.2	rich (reducing)
Sn	4.8	rich (reducing)
Ti	5.2	rich (reducing)

^aBurner head rotated 90° so that the burner slot is perpendicular to the light beam.

^bThe nitrous oxide flow rate is 10.4 L/min for all elements.

burner head. The larger the observation height the longer the analyte's residence time. After optimizing the fuel-oxidant ratio the optimum observation height (Table 68) was determined for each element by observing the light absorbed at various burner heights. The elements Ag, Cu, and Fe required observation heights of 5 mm or less while the optimum observation height for all other elements was observed to be between 8 and 12 mm.

Since atomic absorption analyses are known to be dependent on wear metal particle size, the absorption maxima were determined on samples prepared from metal powders. The analysis of the metal powder suspensions was used to determine what effect the presence of wear metal particulates had on the optimum conditions for wear metal determinations. If metal particulates require longer residence times to vaporize, larger observation heights than those observed for Conostan standards should be required before maximum absorption is observed.

As expected, larger values for the observation heights than those observed for Conostan standards are necessary to analyze metal particles for all wear metals except Cu, Ag, Mg and Mo. The maxima for Cu, Mo and Ag particles were observed at the same observation height as their organometallic counterparts while the maxima for Mg was recorded at lower observation heights than its organometallic counterpart.

e. Interferences

The term interference may be defined as any effect which alters the population of ground state atoms and leads to an error in the determination of the element's concentration. Interferences of importance to wear metal analyses occur in the nebulization process and have to do with sample viscosity and the presence of metallic particles. Effects due to viscosity differences can be minimized by diluting with the appropriate amount of solvent.

The samples and standards are diluted prior to analysis in order to reduce any effects due to viscosity differences between the typical used MIL-L-7808H or MIL-L-23699

TABLE 68

SUMMARY OF THE OPTIMUM OBSERVATION HEIGHTS

<u>Metal</u>	<u>Optimum Observation Height</u> (mm)
Ag	5
Al	12.5
Cr	10
Cu	5
Fe	5
Mg	10-15 (burner head at 90° with respect to beam)
Mo	10
Ni	8
Pb	8
Si	10
Sn	8
Ti	12

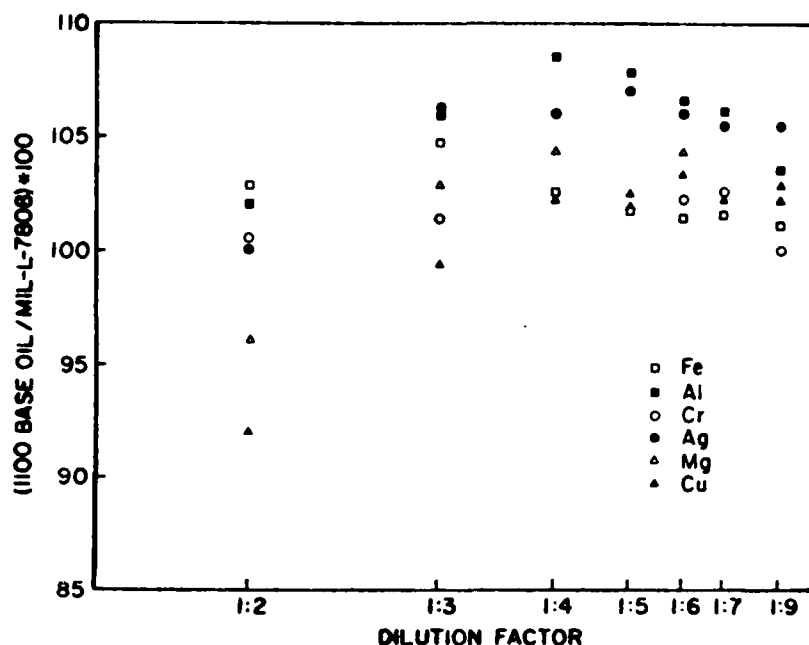


Figure 30. Effect of Dilution on the Absorbances for D20 Conostan Standards in 1100 Base Oil and MIL-L-7808 Ester Oil

synthetic lubricant and the 1100 base oil used in preparing standards. The appropriate dilution factor was determined by preparing standards in MIL-L-7808H ester oil (viscosity = 13.9 cs at 100°F) and 1100 base oil (viscosity = 241 cs at 100°F). The ratio of the absorbance signals of the 1100 base oil/ester oil were plotted against the dilution factors used (dilution factor = 2,3,4,5,6,7 and 9). The elements determined in each oil were Ag, Al, Cr, Cu, Fe and Mg. Figure 30 reveals that a dilution factor of 4 (1 part oil to 3 parts MIBK) is sufficient to minimize any viscosity differences between ester and hydrocarbon oils. To be sure that viscosity differences are minimized a dilution factor of 5 (1 part oil to 4 parts MIBK) is recommended for the analysis of wear metals in lubricating oils.

Another error occurs in the nebulization process when particles of wear metal are present in the lubricating oil. The nebulization process discriminates against large particles and

the efficiency of particle transport has been shown to be inversely proportional to particle size. Wear metal particles larger than 20 μm are not transported to the flame and end up in the drain container. The only solution to the particle problem is to use the acid dissolution procedure described later in this section. The procedure ensures that large particles found in lubricating oils will be detected.

f. Detection Limit

The detection limit takes into account baseline noise and is defined as the concentration that can be "accepted with confidence as genuine and is not suspected to be only an accidentally high value of the blank measure"⁽²⁸⁾. For this work the detection limit is the concentration that yields a signal two (2) times its standard deviation

$$\text{Detection Limit} = \frac{2 \cdot C \cdot \text{S.D.}}{\bar{X}}$$

where C is the concentration of the standard before dilution, S.D. is the standard deviation of the measurements and \bar{X} is the average of the measurements. The significance of 2 S.D. is that at the detection limit, concentrations can be determined at the 95% confidence limit.

For the most part the detection limit is of little concern to the oil laboratory analyst since concentrations below 1 ppm are presently not of concern for wear metal analyses. However, the detection limits do indicate the accuracy obtainable at low concentrations. Also the detection limits (Table 69) of Pb, Si, and Sn are 0.92, 0.65 and 1.60, respectively, which indicate that concentrations of Pb, Si, and Sn below 2 ppm will be difficult to determine.

g. Working Curves

All light absorbing methods, including atomic absorption spectrometry, are based on the Beer-Lambert law which

TABLE 69

DETECTION LIMITS FOR THE ATOMIC ABSORPTION
SPECTROMETRIC ANALYSIS OF WEAR METALS

Element	Detection Limit ppm after 1:4 Dilution
Ag	0.05
Al	0.65
Cr	0.061
Cu	0.075
Fe	0.105
Mg*	0.065
Mo	0.05
Ni	0.31
Pb	0.92
Si	0.65
Sn	1.60
Ti	0.49

* Burner rotated 90° with respect to the
the light beam

states that the intensity of a light beam passing through an absorbing medium decreases exponentially with the number of absorbing atoms. The mathematical expression for this law is:

$$I_x = I_o \cdot 10^{KC}$$

where I_o is the intensity of the entering light beam, I_x the intensity of the emerging beam, C the concentration of absorbing atoms and K a constant which includes variables such as path length and flame temperature. The equation may also be written in logarithmic form:

$$\log \frac{I_o}{I_x} = KC = A$$

where the value of $\log I_o/I_x$ is defined as absorbance (A). In this form, the relationship between the absorbance and concentration is linear, making plotting and interpolation easy. The concentration range in which the law holds is relatively short and is referred to as the "linear working range". With increasing concentration the working curve becomes nonlinear and usually curves toward the concentration axis. The failure of Beer's Law results from an efficiency loss in the absorption process at higher analyte concentrations. For best results the concentrations determined should be within the linear working range of that element. The Figures in Section VII show the working curves established for each of the twelve wear metals using a dilution ratio of 1 part standard to 4 parts MIBK. The working curves for eight metals were linear up to 100 ppm. The working curves for Mg and Cu were linear up to 80 ppm while the working curves for Fe and Cr were linear up to 50 and 60 ppm respectively.

To determine concentrations above the linear region one must use the curve correction controls provided on some P.E. instruments, dilute the solutions to stay on the linear portion

of the working curve, or go to a less sensitive wavelength. Using the curve correction controls it is quite practical to obtain sufficiently accurate concentrations between zero and 100 for all twelve wear metals. To determine concentrations above 100 ppm the solutions should be diluted so that the linear portion of the working curve is used.

3. DEVELOPMENT OF AN IMPROVED ACID DISSOLUTION METHOD

a. Introduction

The main limitation of spectrometric oil analysis is that the spectrometric methods currently used are insensitive to large wear metal particles. The detection of particulate contamination is imperative since the presence of particles is indicative of component wear and the wear particles often accelerate wear processes which degrade component surfaces. To analyze oils containing large wear metal particles (particles greater than 5 μm), a particle dissolution procedure has been developed which yields quantitative recoveries of Al, Cr, Cu, Fe, Mg, Mo, Ni, Pb, Sn and Ti. Improved recoveries of other wear metals, such as Ag, were also evident.

The approach used in developing this method is similar to the ones developed to determine Ti and Mo in lubricating oils. (29,30) A small amount of acid is added to the oil sample before dilution and subsequent AA analysis. The acid mixture employed has been modified so that most wear metals are dissolved. The reaction conditions affecting percent recoveries, precision, and accuracy were studied using both metal powder suspensions and authentic used oils samples. The results of these experiments are presented herein.

b. Optimization of the Acid Dissolution Method for Metal Powders

The HF/HCl mixture used in the titanium procedure was modified to include other wear metals in the procedure. Various mixtures of HF, HCl, HNO_3 and H_2SO_4 were studied with mixtures

of HF, HNO_3 and HCl giving the best results (Fig. 31). The highest recoveries, to date, have been obtained with an acid mixture containing 10% HNO_3 , 10% HF and 80% HCl by weight. Higher percentages of HNO_3 decreased recoveries of Ti, Pb, Si and Mo. (Fig. 32). In the Figures the height of the bars represent the average % recovery and the black portion represents the standard deviation.

Since oil samples are usually heterogeneous mixtures of wear metal particles suspended in oil, the samples should be thoroughly shaken prior to sampling. According to our experiments at least 2 g of sample should be weighed out for analysis in order to minimize any sampling errors.

Experiments designed to determine the optimum reaction temperature, reaction time, and acid amount (Fig. 33) were carried out using the metal powder suspensions. The optimum reaction conditions for the metal powder suspensions were found to be 0.4 g acid/2 g oil with ultrasonic agitation for 5 min at 65°C.

The utilization of a surfactant, enables ester as well as hydrocarbon oils and hydraulic fluids to be analyzed by the recommended procedure. The surfactant effectively provides a homogeneous mixture of oil, acid and solvent which can be easily analyzed by AAS. The surfactant employed was Neodol 91-6 which is an ethoxylated primary alcohol obtained from Shell Chemical Co. Neodol 91-6 has the chemical formula $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_6$ where R is C_9H_{19} , $\text{C}_{10}\text{H}_{21}$ or $\text{C}_{11}\text{H}_{23}$ (linear). The solvent/surfactant ratio used to provide a homogeneous solution was 3 parts MIBK to 1 part Neodol 91-6. Other surfactants were tried but did not give acceptable results.

The dilution factor was determined by comparing absorption signals observed for standards prepared in MIL-L-7808H ester oil with standards prepared in heavy (245) hydrocarbon oil. The ratio of the absorbance signals of the heavy hydrocarbon oil/ester oil were plotted against the dilution factors used.

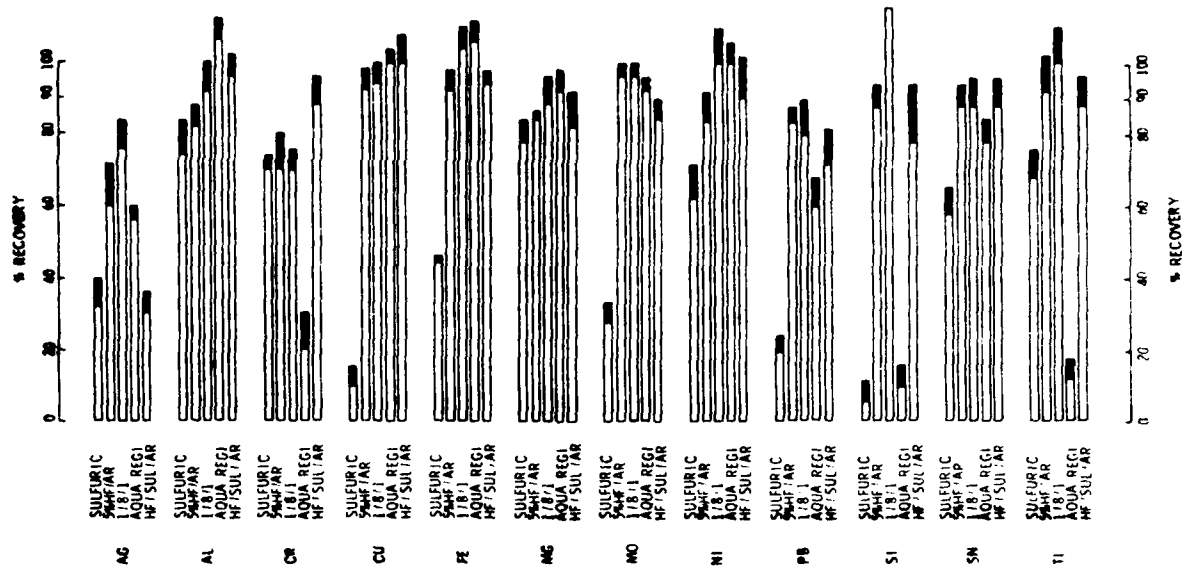


Figure 31. Effect of Acid Type on Percent Recovery.

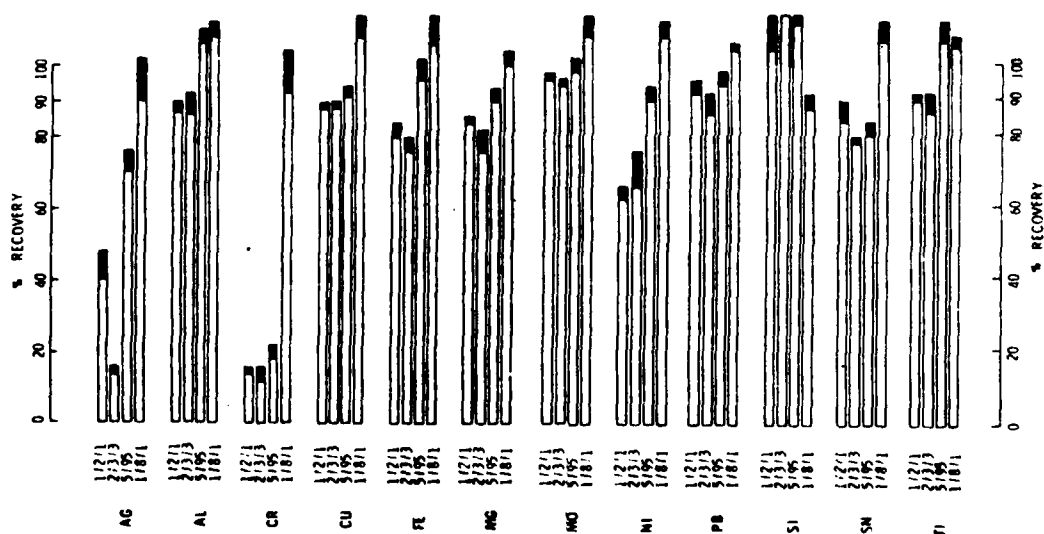


Figure 32. Effect of the Ratio of HNO_3 to HCl to HF on Percent Recovery.

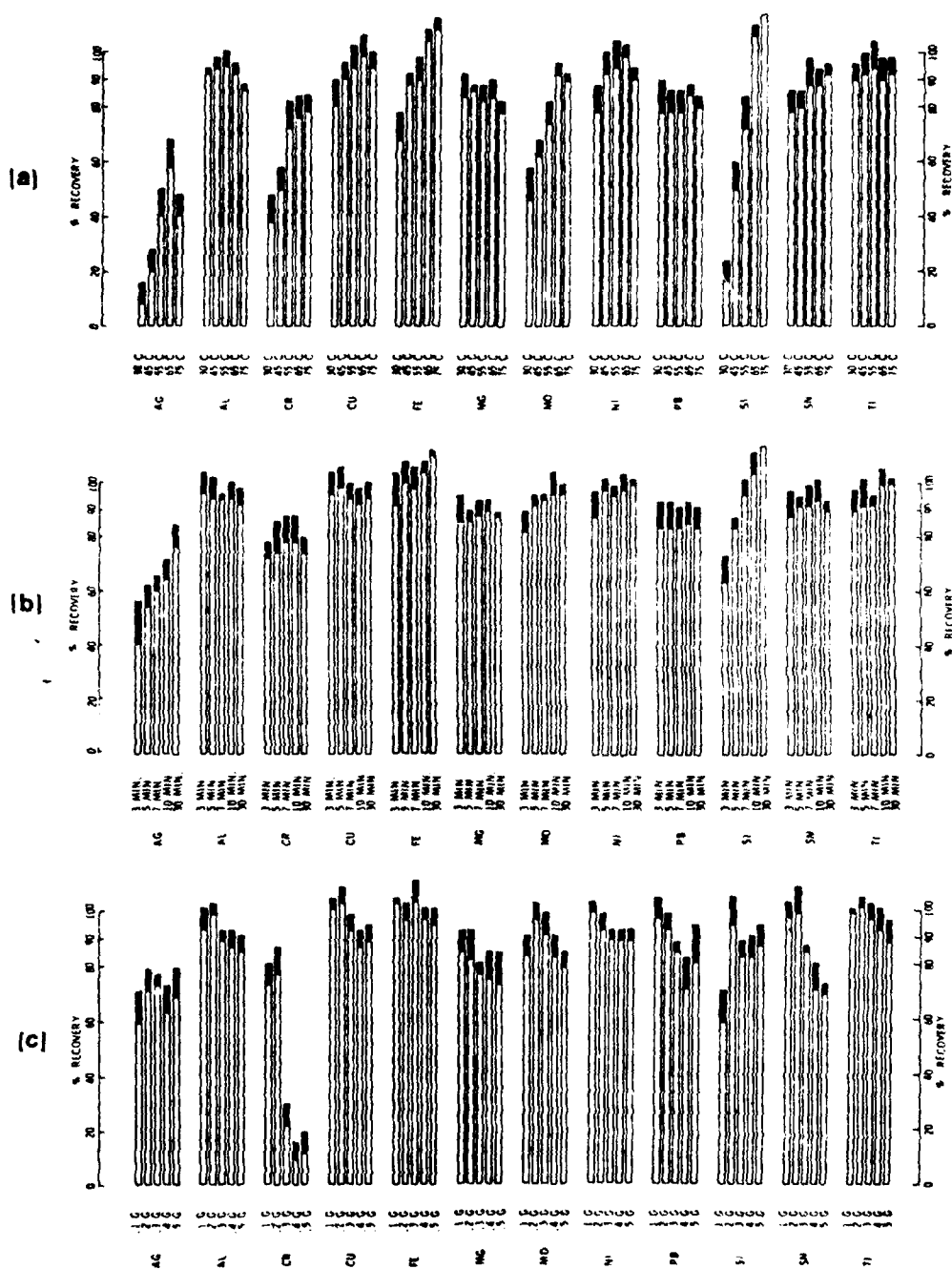


Figure 33. Effect of Reaction Temperature (a), Reaction Time (b) and Acid Amount (c) on Percent Recovery.

Absorption signals were measured for Ag, Al, Cr, Cu, Fe, Mg and Ni. Figure 34 reveals that a dilution factor of 7 (1 part oil to 6 parts solvent) was required to minimize viscosity differences between ester and hydrocarbon oils.

Using the optimum reaction conditions the metal powders suspended in oil were analyzed and compared to values determined by direct analysis. The percent recoveries obtained are shown in Fig. 35. The percent recoveries ranged from 2-48% when analyzed directly but ranged from 89-102% using the acid dissolution procedure. The acid dissolution procedure also dramatically improved the recovery of Ag (75% of theoretical). The precision of the method is good ranging from 2-12% for all the elements analyzed.

c. Optimization of the Acid Dissolution Method for Used Lubrication Oils

The optimization experiments were repeated using authentic used oil samples. Used oil samples typically contain a lower concentration of wear metal than the metal powder suspensions; therefore, the used oil samples can be analyzed with less rigorous reaction conditions. In addition to lower concentrations, the elemental composition of the wear metal particles is different than the elemental composition of the pure metal powders. The wear metals found in used oils can be alloys, oxidized metals or organometallic in nature, etc.

Upon analysis of used oils under various conditions, 5 min was still found to be the optimum reaction time (Fig. 36). However, the optimum reaction temperature was found to vary with the method of agitation, the composition of the oil, and the wear metal being analyzed (Fig. 37). The hydrocarbon oils require vortex mixing ("Maxi Mix") to be effectively analyzed at room temperature (25°C). The use of ultrasonic agitation (ULT) required a reaction temperature of 40°C to be effective with hydrocarbon oils. The method of agitation or reaction temperature did not have any effect on wear metals in ester oils. The recovery of Mo is the exception and requires a reaction temperature of 65°C for quantitative recovery.

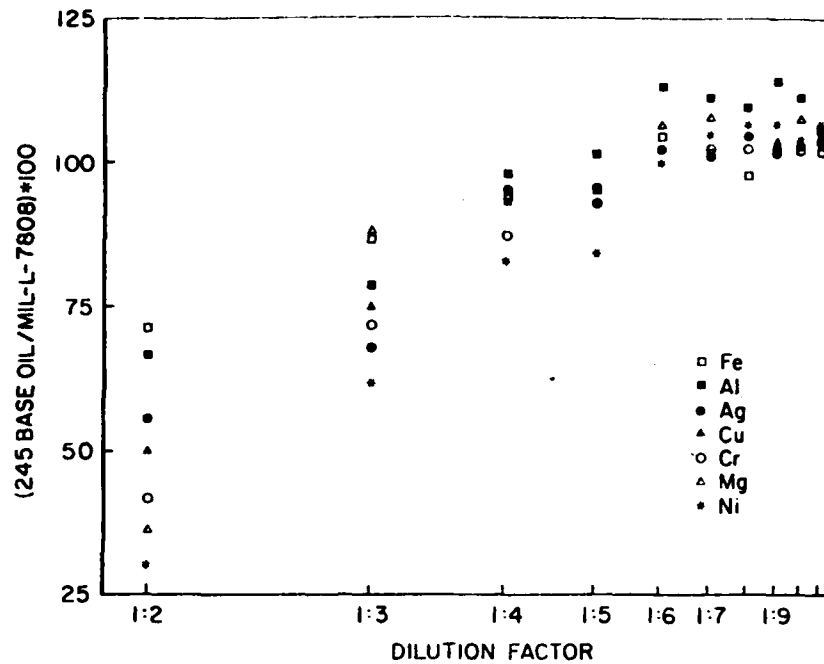


Figure 34. Effect of Dilution on the Absorbances of D20 Conostan Standards in 245 Base Oil and in MIL-L-7808 Ester Oil for the Acid Dissolution Method.

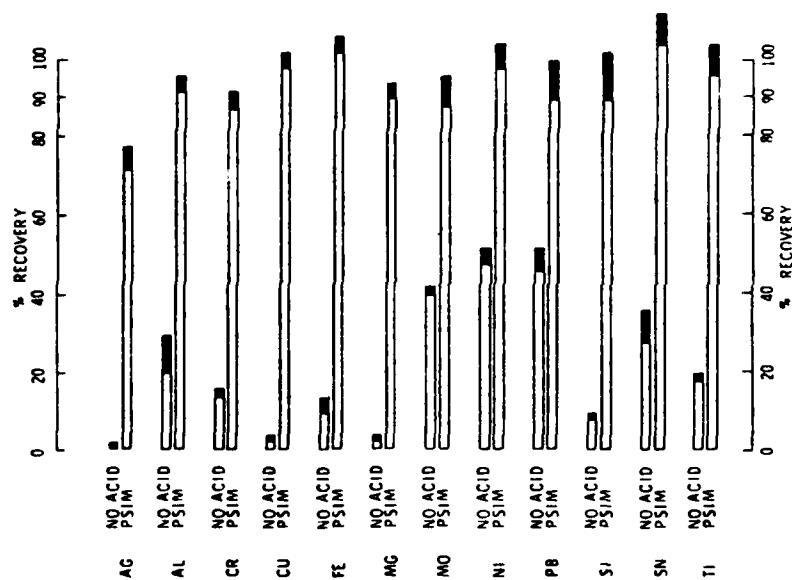


Figure 35. Comparison of Percent Recoveries Determined by Direct Analysis and by the Acid Dissolution Method.

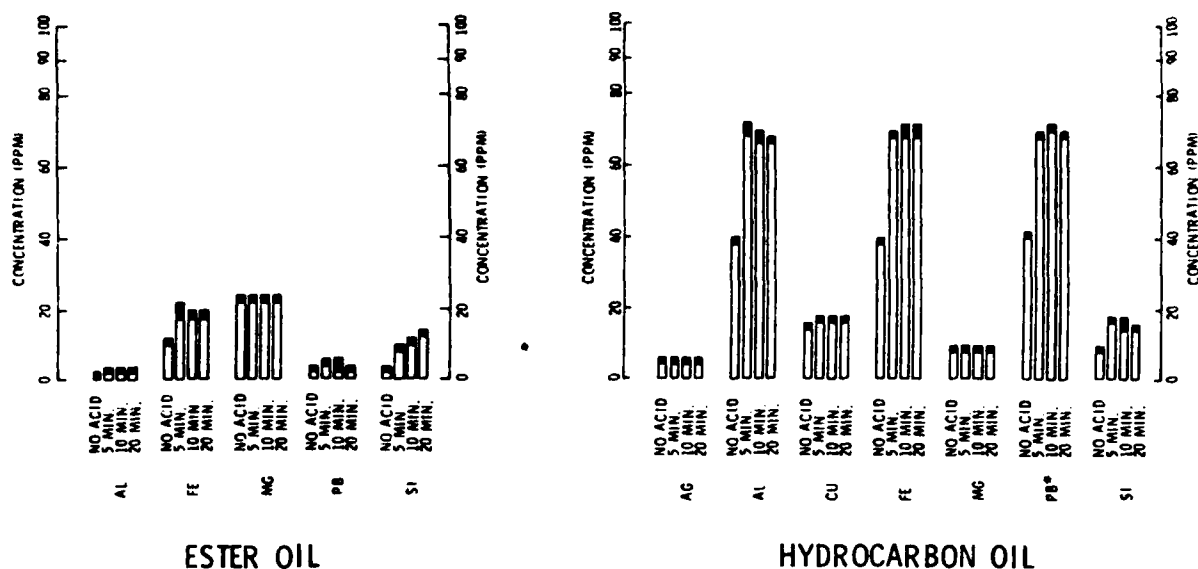


Figure 36. Effect of Reaction Time on Metal Concentrations Determined for Used Oil Samples.

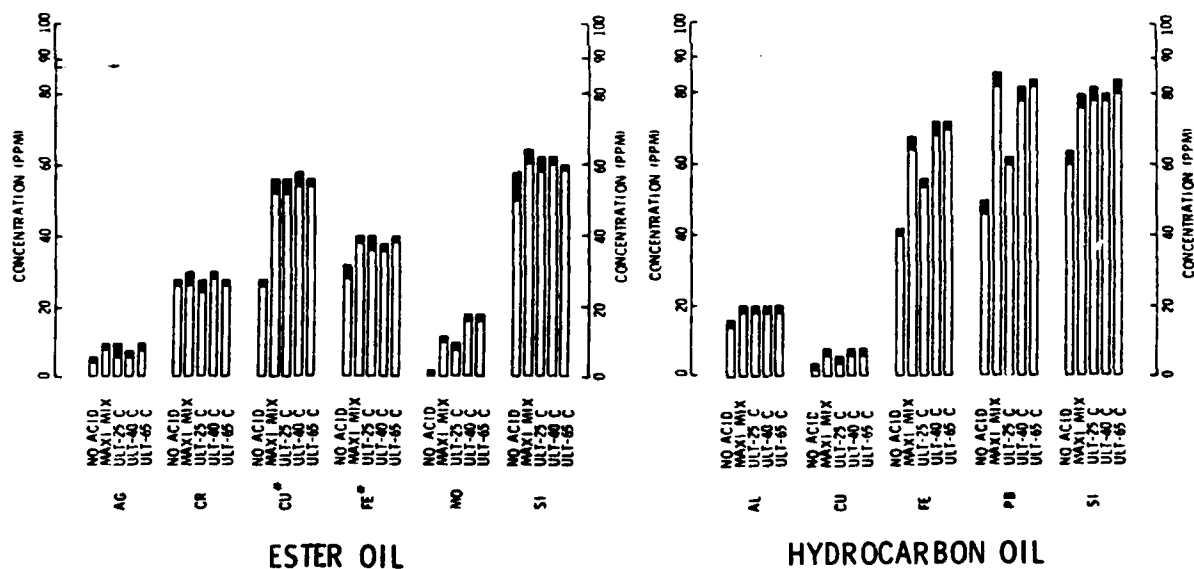


Figure 37. Effect of Reaction Temperature on Metal Concentrations Determined for Used Oil Samples.

To confirm the observation that vortex mixing at room temperature or ultrasonic agitation at 40°C gives similar results to ultrasonic agitation at 65°C twenty used oil samples containing large particles were analyzed using all three procedures. The values determined using ultrasonic agitation at 65°C were plotted against the average value determined using both vortex mixing at room temperature and ultrasonic agitation at 40°C. The concentrations determined for Ag, Al, Cr, Cu, Fe and Mg were used for comparison. If the three methods produce equal results the slope would be 1.0 and the variance would be small. Both conditions were met as shown in Figure 38, verifying that excellent results can be obtained at temperatures lower than 65°C. In fact, 25°C is adequate if the vortex mixer is used.

Another method used to verify the analytical results was to compare the results determined by emission and by atomic absorption spectrometry. Authentic used oil samples were treated by the acid dissolution method and then analyzed by emission and AA spectrometers. In all cases the AA determined concentrations agreed with the emission values (Fig. 39) as determined on the dc plasma (DCP) instrument (Spectraspan III, Spectrametrics, Inc.).

A few samples containing only small particles and low wear metal concentrations were analyzed directly and by the acid dissolution method. The concentrations determined by the two methods were identical verifying that the higher concentrations obtained on particulate contaminated oil samples are accurate and the values are not enhanced due to the acid present.

As a final test of the importance of using the acid procedure, ninety used oil samples were analyzed using the acid procedure and compared to the concentrations determined by direct analysis. The results were plotted for each of the twelve wear metals; Ag, Al, Cr, Cu, Fe, Mg, Mo, Ni, Pb, Si, Sn and Ti. The slopes and variances of the elements with concentrations above 2 ppm in 15 or more samples are listed in Table 70. Table 71 contains examples where the acid method gives significantly improved wear metal recoveries.

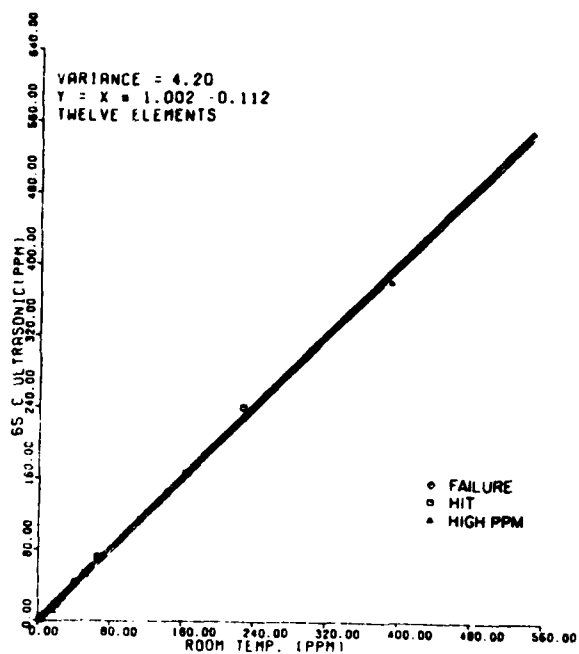


Figure 38. Comparison of Metal Concentrations Determined at Room Temperature and at 65°C.

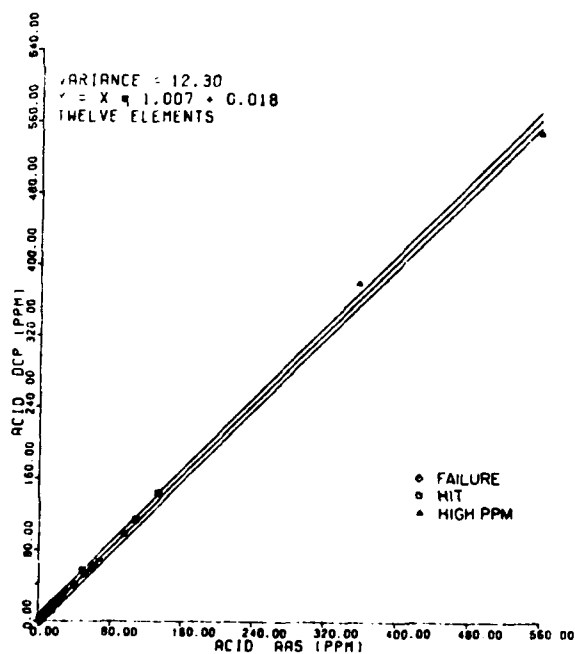


Figure 39. Comparison of Metal Concentrations Determined by AAS and by the DC Plasma (DCP) Emission Spectrometer.

TABLE 70

THE SLOPE AND VARIANCE FROM PLOTS OF THE METAL
CONCENTRATIONS DETERMINED USING THE ACID DISSOLUTION
PROCEDURE vs DIRECT ANALYSIS

<u>Element</u>	<u>No. of Samples</u>	<u>Slope</u>	<u>Variance</u>
Ag ¹	19	0.65	1.54
Al ²	52	0.85	3.89
Cr ²	68	0.69	0.41
Cu ²	79	0.63	2.78
Fe ²	188	0.76	10.84
Mg ²	75	0.99	3.76
Ni ¹	34	0.62	0.34
Pb ¹	45	1.03	2.85
Ti ²	3	0.29	-

¹Direct D.C. Plasma Emission Analysis

²Direct AAS Analysis

TABLE 71

A COMPARISON OF METAL CONCENTRATIONS DETERMINED BY
DIRECT AAS ANALYSIS AND BY THE ACID DISSOLUTION METHOD

Sample No.	Element	AAS (ppm)	ADM (ppm)	ADM-AAS (ppm)	% Particles ¹
F4	Fe	5.0	9.1	4.1	45.0
F6	Fe	11.7	31.0	19.3	62.2
	Ni	0.2	1.8	1.6	88.8
	Si	7.5	21.4	13.9	64.9
	Al	1.4	3.0	1.6	53.3
	Ag	2.0	3.4	1.4	41.2
F20	Fe	0.6	4.2	3.6	85.7
F37	Fe	3	15.1	12.1	80.1
	Cu	2	8.6	6.6	76.7
	Ag	0.1	3.6	3.5	97.2
H33	Ni	6.3	12.9	6.6	51.2
	Ti	11.6	16.0	4.4	27.5
H48	Fe	105	370	265	71.6
	Cu	136	560	424	75.7
	Mo	0.1	15.5	15.4	99.4
R4	Al	12.2	15.6	3.4	21.8
	Mg	12.4	17	5.0	29.4
	Cu	3.8	5	1.2	24.0
R12	Fe	6.1	13.4	7.3	54.5
	Cu	4.2	7.4	3.2	43.2
	Al	0.3	1.6	1.3	81.3
	Ag	0.5	1.5	1.0	66.7
	Si	2.7	5.2	2.5	48.1

$$^1\% \text{ Particles} = \left(\frac{\text{ADM-AAS}}{\text{ADM}} \right) * 100$$

The slopes listed in Table 70 are all below 1.0 because the acid procedure significantly improves the recoveries of wear metal. The slopes together with the data listed in Table 71 indicates that direct analysis of the oil does not give a true indication of the wear metal concentration. Even the concentration of Ag is increased by the acid dissolution method. For all oil samples analyzed the addition of acid was never observed to be detrimental. Therefore, once the acid reaction has been carried out, the resulting solution can be used to analyze for all wear metals of interest.

In fact, the difference between the results determined by direct analysis and the results determined by the acid dissolution method can be used as a diagnostic test for the presence of particulate contamination. A concentration of particles greater than 20-30% of the total wear metal concentration indicates the presence of metal particles larger than 1-3 μm and abnormal engine wear. Many of the "FAILURE" samples tested contained significant concentrations of particulate contamination which indicates that wear particles were generated during or before engine failure. Two "ROUTINE" samples were received which contained particles. A follow up on sample R4 indicated that the engine later failed undetected by the Oil Analysis Program.

Figure 40 shows the comparison between direct AAS analysis and the acid dissolution method for Fe. Only FAILURE, HIT and HIGH PPM samples containing less than 30 ppm Fe were plotted. The figure shows that a significant number of these samples contain metal particulates that were not detected by direct AAS analysis. Perhaps some of the FAILURE'S could have been avoided had the presence of wear particles been detected.

When the acid dissolution method is used a 5 g sample of oil reacted with 1 g of acid for 5 min and then diluted with 29 g of solvent will give 35 g of solution. The resulting amount of solution should be adequate to analyze for all 12 wear metals

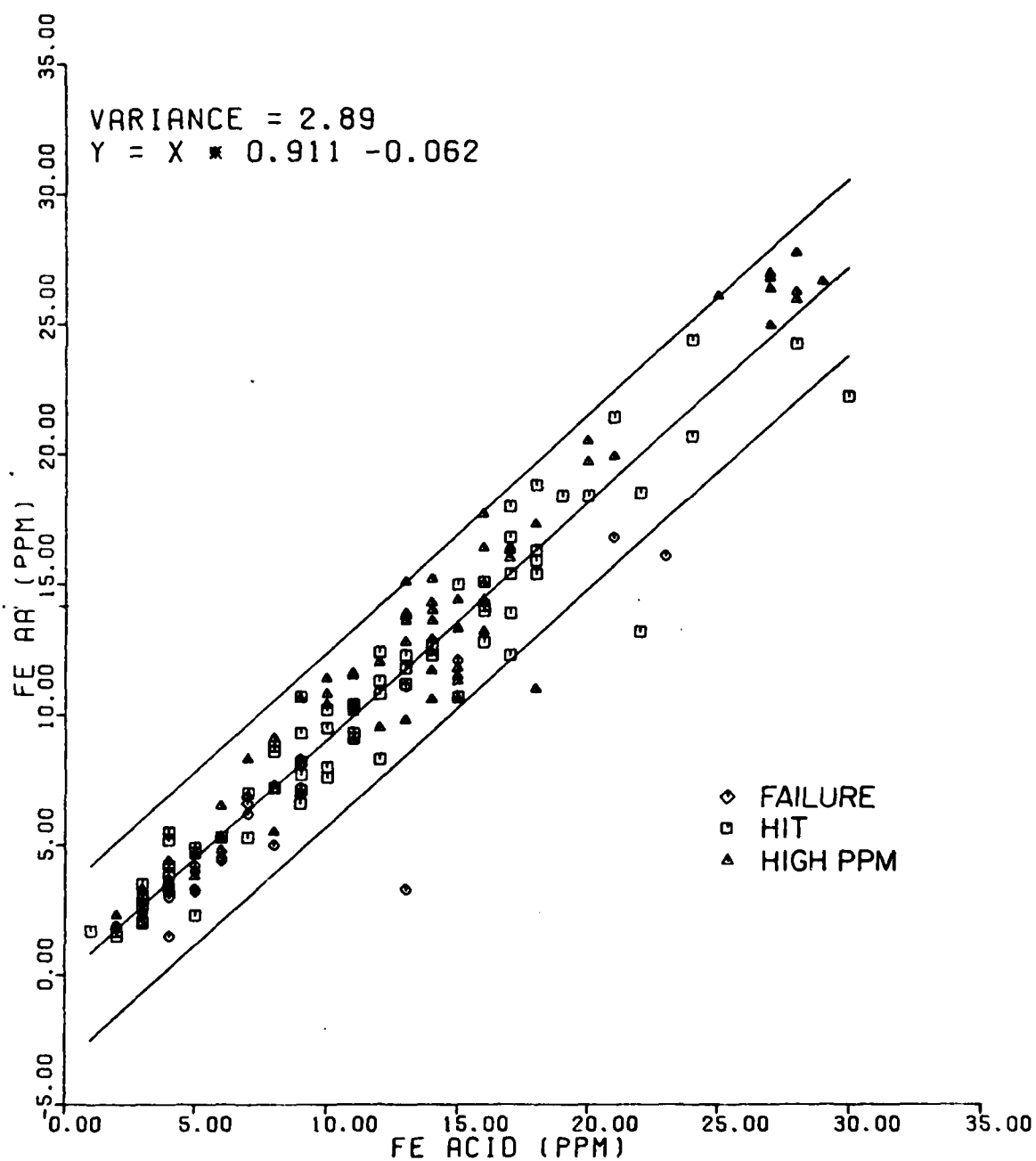


Figure 40. Plot of Fe Determined by the Acid Dissolution Method vs. Fe Determined by Direct AA Analysis.

usually determined by AAS. If an accurate Mo determination is required a reaction temperature of 65°C will be required; otherwise, a reaction temperature of 25°C is adequate.

4. RECOMMENDATIONS

Although the majority of used turbine engine lubricants will not contain large wear metal particles, detecting their presence can be important in predicting abnormal engine wear. The acid dissolution method (ADM) was developed so that wear metal particulates could be quantitatively analyzed. The capability to detect large wear metal particles should improve JOAP's ability to predict turbine engine failure.

Since there is not a currently available test procedure which can be used to determine the presence of metallic particles, we recommend that the acid dissolution method be field tested by analyzing all used oil samples received in AA equipped OAP laboratories by both the usual method and by the acid dissolution method. The questions which should be answered during the field test period include: 1) Is detecting the presence of large particles important in predicting engine failure? 2) Are current AAS wear metal guidelines acceptable for samples analyzed by the ADM? and 3) Is the method acceptable to the AAS operators in Air Force AA equipped laboratories?

We also recommend that the difference between the concentrations determined from direct analysis and the ADM be tabulated for each sample. Our limited experience has shown that when concentrations determined by the acid dissolution method are 20-30% higher than those determined by direct analysis the oil sample contains an unusually high concentration of large wear metal particles and indicates that abnormal wear is occurring in the engine.

The recommended conditions for analyzing wear metals by atomic absorption spectrometry are given in Section VII. We recommend that the acid dissolution method be used for Ti and Mo since particulates of these metals are very difficult to analyze by flame AA methods.

5. EXPERIMENTAL

a. Instrumentation

All atomic absorption analyses were performed on a Perkin-Elmer 305B atomic absorption spectrophotometer equipped with a nitrous oxide burner head (5 cm slot). The fuel (acetylene)/oxidant (nitrous oxide) flowmeter settings were obtained directly from the flowmeters of the burner control box (Perkin-Elmer Model 303-0678). The settings were converted into flow rates in L/min using Perkin-Elmer's plot of flowmeter reading vs. L/min (14). The absorbance signal was fed into a Linear Instruments Corp. Model 112 strip chart recorder. Ten chart divisions are equivalent to one absorbance unit. Therefore, absorbance was obtained from the relationship:

$$\text{Absorbance} = \text{chart divisions} / (10 \cdot \text{scale expansion})$$

The relative absorbance was calculated from the equation:

$$\text{Relative Absorbance} = \frac{(\text{sample absorbance} \cdot 100)}{\text{standard absorbance}}$$

The experimental conditions are summarized in Table 72.

b. Apparatus

Used oils and standards, etc., were weighed on a Mettler Gram-Atic analytical balance, a Mettler P1200 top loading balance or a Sartorius 1204 MP top loading balance.

The samples were agitated using a Blackstone heated ultrasonic bath or a Thermolyne Maxi Mix vortex mixer. The Maxi Mix mixer was fitted with a foam container which allowed two samples to be agitated simultaneously.

c. Reagents

All solvents used were reagent grade. Solvents required are methyl isobutyl ketone, acetone, and distilled water.

Standards were supplied by the JOAP TSC, NAS, Pensacola, Florida.

TABLE 72
SUMMARY OF INSTRUMENTAL CONDITIONS FOR WEAR METAL ANALYSES

Instrument	Perkin-Elmer 305B
Burner Head	Perkin-Elmer 303-0419
Burner Control Box	Perkin-Elmer 303-0678
Grating	UV
Nitrous Oxide	
Tank Regulator	40 psig
Burner Control	30 psig
Flowmeter Setting	5.0 (center of ball)
Flow Rate	10.4 L/min
Acetylene	
Tank Regulator	14 psig
Burner Control	8 psig

<u>Element</u>	<u>Wavelength</u>	<u>Slit (nm)</u>	<u>Current (m.a.)</u>	<u>Fuel^c Flowmeter Setting</u>	<u>Fuel Flow (L/min)</u>
Ag	328.1	0.7	30 ^b	2.0	2.4
Al	309.3	0.7	30 ^b	3.5	4.4
Cr	357.9	0.7	25	3.5	4.4
Cu	324.7	0.2	30 ^b	2.0	2.4
Fe	248.2	0.2	30 ^b	3.5	4.4
Mg ^a	285.4	0.7	30 ^b	3.0	3.7
Mo	313.6	0.7	30	4.0	5.2
Ni	341.5	0.2	25	3.8	4.8
Pb	283.3	0.7	12	3.5	4.4
Si	251.6	0.2	40	4.0	5.2
Sn	286.3	0.7	30	3.8	4.8
Ti	365.4	0.2	40	4.0	5.2

^aBurner head turned 90° with respect to light beam path

^bMultielement lamp of Ag, Al, Cu, Fe and Mg was used

^cCenter of steel ball

The surfactant used in the acid procedure is Neodol 91-6 and was obtained from the Shell Chemical Co., Middleburgh Heights, Ohio 44130. The solvent referred to as Neodol 91-6/MIBK was prepared by mixing 25 g of Neodol 91-6 with 75 g of MIBK for each 100 g of solvent.

All acids used were concentrated reagent grade acids.

Metal powders were greater than 99% pure and obtained from Research Organic/Inorganic Chemical Corp., Sun Valley, California 91352. The Ag powder was obtained from Vacuum Metallurgical Company (VMC), Tokyo, Japan.

The mixture of HF/HNO₃/HCl was prepared by mixing 10 g concentrated HF with 10 g concentrated HNO₃ then adding 80 g of concentrated HCl.

d. Calibration Standards

Oil calibration standards supplied by the JOAP TSC, NAS, Pensacola, FL, contain the 12 elements analyzed by atomic absorption spectrophotometry. Standard solutions were prepared by dissolving each desired standard in MIBK using 4 parts MIBK (by weight) for each part standard.

The calibration standards for the acid dissolution procedure were prepared from the standards supplied by the JOAP TSC. Each gram of standard is diluted with 0.2 g acid (HF/HNO₃/HCl) and 5.8 g of the Neodol/MIBK solvent. Five grams of standard requires 1 g of acid and 29 g of Neodol 91-6/MIBK solvent for a final dilution ratio of 5:1:29 (oil/acid/solvent).

The standards used to determine viscosity effects were prepared from 900 ppm Conostan standards in 245 base oil as formerly supplied by the JOAP TSC. Standards with concentrations of 100 ppm were prepared by diluting the 900 ppm standard with the appropriate amount of MIL-L-7808H (Mobil) ester oil, 1100 base oil, or 245 base oil. The standards were diluted with MIBK or with acid and solvent (Neodol 91-6/MIBK) prior to AA analyses.

e. Metal Powder Suspensions

To determine the effect of metal particulates on the optimum observation height, suspensions of metal powders were prepared. Each metal powder was weighed out and suspended in MIL-L-7808H (Mobil) ester oil to prepare suspensions containing 100 ppm of metal. Single element suspensions of Ag, Al, Cr, Cu, Fe, Mg, Mo, Ni, Pb, Sn and Ti were prepared. The Al and Fe metal powders were sifted through a 5 μ m filter before use. The other metal powders were used as received.

A multi-element suspension was prepared by weighing equal amounts of each metal powder into a 32 oz polyethylene bottle and diluting with MIL-L-7808H (Mobil) ester oil. In this manner a suspension containing 100 ppm of each metal was prepared.

f. Dilution Factor - Effect of Oil Viscosity

(1) Direct Analysis

For the determination of the optimum dilution ratio, standards prepared with MIL-L-7808H (Mobil) were compared with standards prepared with heavy hydrocarbon base oils. In this particular case D12-100 prepared with MIL-L-7808H (Mobil) was compared with D12-100 prepared with 1100 base oil at various dilution ratios. The samples were prepared so that the concentration remained constant (12 ppm) and the dilution factor was the only variable. Each sample was prepared as follows:

<u>Dilution Ratio</u>	<u>Grams of D12-100</u>	<u>Grams of Unused Oil</u>	<u>Grams of MIBK</u>
1:1	1.2	3.8	5.0
1:2	1.8	3.2	10.0
1:3	2.4	2.6	15.0
1:4	3.0	2.0	20.0
1:5	3.6	1.4	25.0
1:6	4.2	0.8	30.0
1:7	4.8	0.2	35.0

A D12-100 calibration standard diluted 1:5 with MIBK was used to optimize the instrumental conditions prior to analyzing the above samples. The two samples prepared at each dilution ratio were then analyzed one after the other for direct comparison. The results were reported as follows:

$$R = \frac{\text{absorbance of D12 in 1100 base oil} \cdot 100}{\text{absorbance of D12 in MIL-L-7808H (Mobil)}}$$

(2) Acid Dissolution Method

The effect of viscosity on the determination of metals using the acid dissolution procedure was also determined. In a manner similar to the preparation of the above samples, D12-300 calibration standards (one prepared with MIL-L-7808H (Mobil) and one prepared with 245 base oil) were diluted with solvent and oil as follows:

<u>Dilution Factor</u>	<u>Grams of D12-300</u>	<u>Grams of Unused Oil</u>	<u>Grams of Neodol 91-6/MIBK</u>	<u>Grams of Acid</u>
1:2	0.6	4.4	9.0	1.0
1:3	0.8	4.2	14.0	1.0
1:4	1.0	4.0	19.0	1.0
1:5	1.2	3.8	24.0	1.0
1:6	1.4	3.6	29.0	1.0
1:7	1.6	3.4	34.0	1.0
1:8	1.8	3.2	39.0	1.0
1:9	2.0	3.0	44.0	1.0
1:10	2.2	2.8	49.0	1.0
1:11	2.4	2.6	54.0	1.0

After dilution with Neodol 91-6/MIBK the concentration of metal in each solution was constant (12 ppm) and the dilution factor was the only variable.

A D12-100 calibration standard diluted with acid (0.2 g/g standard) and Neodol 91-6/MIBK solvent (5.8 g/g standard) was used to optimize the instrumental conditions. The two samples at each dilution factor (one prepared with MIL-L-7808H (Mobil) ester oil and the other prepared with a 245 base oil) were

analyzed one after the other for direct comparison. The results were reported as above.

g. Calibration of Observation Height

The observation height is defined as the perpendicular distance between the top of the burner head and the center of the aligned light beam. The observation height was determined directly using a 4-cm block which was marked in millimeter increments. The block was placed on the burner head and the distance from the head to the center of the light beam recorded in mm.

The vertical burner height is controlled on the PE305B with a vertical adjust knob which has a scale marked from 0 to 20. Using the above block the scale was calibrated so that the observation height could be determined in mm from the scale reading on the adjust knob. The position where the light beam and the burner head intersect was defined as zero.

h. Optimization of Fuel/Oxidant Ratios and Observation Height

The optimum fuel/oxidant ratio and observation height were obtained for each element using a D12-100 calibration standard diluted 1:4 with MIBK. The absorption was maximized by adjusting the fuel flow rate while leaving the oxidant flow constant at 10.4 L/min. The optimum observation height was found by varying the burner head height and recording the absorbance. The observation height was plotted vs absorbance and the optimum observation height taken as the point where maximum absorbance was observed.

The above procedure was repeated for each element using the 100 ppm single element powder suspensions.

The procedure was repeated again using the calibration standards prepared for the acid dissolution procedure. The optimum conditions observed for the acid containing samples were identical to the conditions determined for the D12-100 standards above.

i. Detection Limits

The detection limits were determined using calibration standards prepared at concentrations of 3, 1, 0.1 and 0.01 ppm. The standards were prepared by diluting a D12-3 standard with the appropriate amount of MIL-L-7808H (Mobil) ester oil. Each standard and the blank was diluted 1:4 with MIBK and analyzed. The blank was MIL-L-7808H (Mobil) ester oil.

j. Optimizing the Acid Dissolution Procedure

The initial optimization experiments were carried out on the multi-element metal powder suspension. The reaction variables investigated were 1) acid mixture composition, 2) acid quantity, 3) reaction time, 4) reaction temperature, 5) sample size and 6) homogenizing diluent. While each variable was being optimized the other conditions were held constant. The optimum conditions chosen were based on the maximum recoveries of all wear metals present.

After the method was optimized to give excellent results for the metal powder suspensions, the variables were reinvestigated using turbine engine oil samples known to contain metallic particles.

All analyses were carried out in triplicate using emission spectroscopy as well as atomic absorption spectroscopy for analyses. The results are reported as percent recovery defined according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Avg Metal Concentration Measured}}{\text{Theoretical Metal Concentration}} * 100$$

k. Summary of Acid Dissolution Method

The optimum method for analyzing turbine engine lubricants by the acid dissolution procedure is as follows:

1. Weigh out a 2 g (or larger) aliquot of the used oil sample in a one ounce polyethylene bottle equipped with a screw cap.
2. Add 0.4 g (0.2 g/g of oil) of the HF/HNO₃/HCl acid mixture.

3. Screw on cap and shake for 10 sec.
4. Agitate for 5 min on a vortex mixer.
5. Dilute with 11.6 g (5.8 g/g of oil) Neodol 91-6/MIBK solvent.
6. Analyze by AA.

A heated ultrasonic bath can also be used to give equally excellent results. Substitute step 4 above with:

4. Agitate for 5 min in an ultrasonic bath which has been heated to $40 \pm 5^{\circ}\text{C}$.

The quantitative recovery of molybdenum requires a higher reaction temperature. Therefore, if an accurate Mo analysis is required substitute step 4 above with

4. Agitate for 5 min in an ultrasonic bath which has been heated to $65 \pm 5^{\circ}\text{C}$.

The above procedure gives 12 g of sample which is sufficient to analyze for 6 elements by AA. If more elements are to be analyzed a larger aliquot of used oil should be weighed out.

SECTION VII
RECOMMENDED PROCEDURES FOR WEAR METAL DETERMINATIONS

1. STANDARD CONDITIONS FOR SILVER

a. Standard Solutions

Oil calibration standards supplied by the JOAP TSC, NAS, Pensacola, FL, contain silver. The standard solutions are prepared by dissolving each desired standard in MIBK using 4 parts (by weight) MIBK for each part (by weight) standard. Standard solutions should be freshly prepared each day the analyses are to be run.

b. Operating Parameters

Instrument	Atomic Absorption
Wavelength	328.1 nm
Grating	UV
Slit Setting	0.7 nm (0.2 nm)
Light Source	Hollow Cathode Lamp
D.C. Current	Multi-element 30 m.a. Single-element 12 m.a.
Flame	Nitrous Oxide-acetylene
N ₂ O Flowmeter Setting	5.0 (10.4 L/min)
Acetylene Flowmeter Setting (Steel ball)	2.0 (2.4 L/min) (oxidizing flame)
Observation Height	5 mm
Linear Working Range	0 to 100 ppm
Detection Limit	0.05 ppm

c. Notes

With multi-element lamps containing copper there is a potential interference from the 327.4 nm copper line, therefore, a slit width of 0.2 nm should be used with a multi-element lamp which contains Cu.

The usual used oil sample will contain less than 10 ppm silver. Therefore, it is recommended that the working curve be determined between zero and 10 ppm with the 10 ppm standard reading full scale. It is important to determine silver accurately

at low concentrations since 3 to 5 ppm is the threshold criteria for most turbine engines.

d. Other Analytical Lines

<u>Wavelength</u>	<u>Slit</u>	<u>Relative Sensitivity</u>
328.1 nm	0.7 nm	1.0
338.3 nm	0.7 nm	1.9

Figures 41 and 42 show the working curve and the effect of observation height for AA determinations of silver.

2. STANDARD CONDITIONS FOR ALUMINUM

a. Standard Solutions

Oil calibration standards supplied by the JOAP TSC, NAS, Pensacola, FL, contain aluminum. The standard solutions are prepared by dissolving each desired standard in MIBK using 4 parts (by weight) MIBK for each part (by weight) standard. Standard solutions should be freshly prepared each day the analyses are to be run.

b. Operating Parameters

Instrument	Atomic Absorption
Wavelength	309.3 nm
Grating	UV
Slit Setting	0.7 nm
Light Source	Hollow Cathode Lamp
D.C. Current	Multi-element 30 m.a. Single-element 25 m.a.
Flame	Nitrous Oxide - Acetylene
N ₂ O Flowmeter Setting	5.0 (10.4 L/min)
Acetylene Flowmeter Setting (Steel ball)	3.5 (4.4 L/min) Reducing Flame (rich, red)
Observation Height	12.5 mm
Linear Working Range	0 to 100 ppm
Detection Limit	0.6 ppm

c. Notes

The usual used turbine engine lubricant will contain less than 10 ppm Al. However, some samples may contain as high

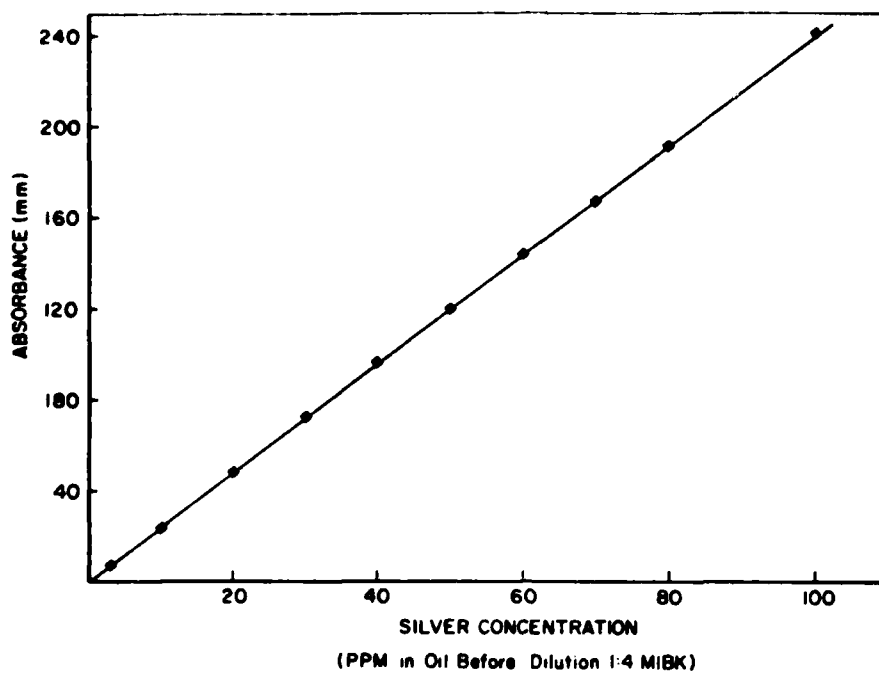


Figure 41. Working Curve for Silver.

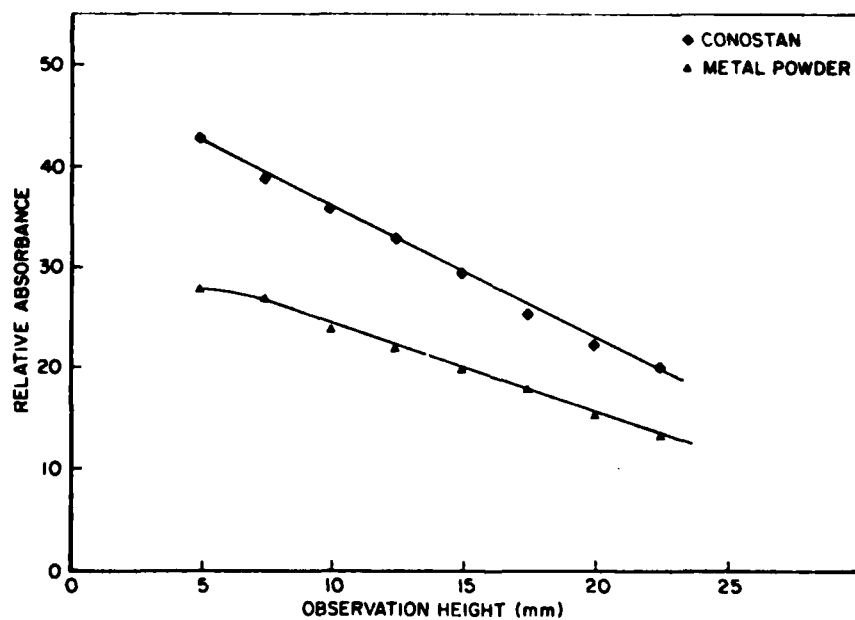


Figure 42. Effect of the Observation Height on the Absorbance of Silver.

as 50 ppm Al. Therefore, it is recommended that the working curve be determined using zero and 50 ppm standards with the 50 ppm standard reading full scale. The threshold value for most turbine engines lies between 3 and 8 ppm for Al.

d. Other Analytical Lines

<u>Wavelength</u>	<u>Slit</u>	<u>Relative Sensitivity</u>
309.27 nm } 309.28 nm }	0.7 nm	1.0
396.2	0.7 nm	1.1
308.2 nm	0.7 nm	1.6
394.4 nm	0.7 nm	2.4
237.31 nm } 237.34 nm }	0.2 nm	6.3
237.6 nm	0.2 nm	6.3
257.51 nm } 257.54 nm }	0.2 nm	8.1
256.8 nm	0.2 nm	12.6

Figures 43 and 44 show the working curve and the effect of observation height for AA determination of aluminum.

3. STANDARD CONDITIONS FOR CHROMIUM

a. Standard Solutions

Oil calibration standards supplied by the JOAP TSC, NAS, Pensacola, FL, contain chromium. The standard solutions are prepared by dissolving each desired standard in MIBK using 4 parts (by weight) MIBK for each part (by weight) standard. Standard solutions should be freshly prepared each day the analyses are to be run.

b. Operating Parameters

Instrument	Atomic Absorption
Wavelength	357.9 nm
Grating	UV

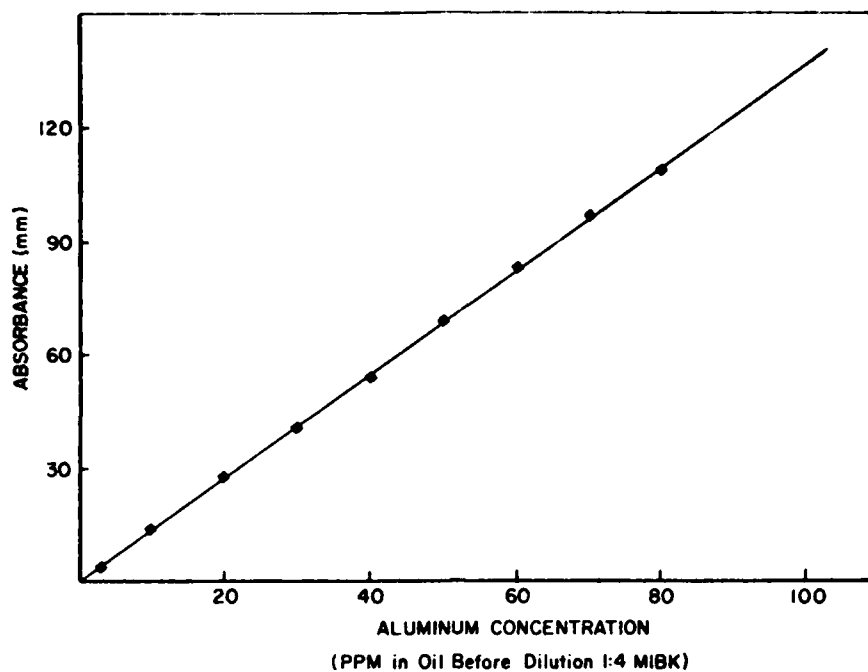


Figure 43. Working Curve for Aluminum.

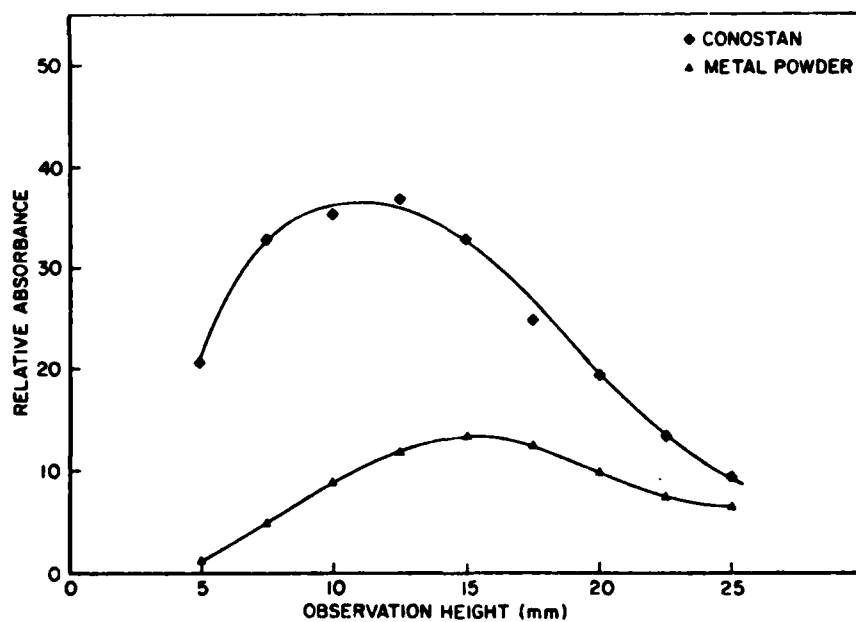


Figure 44. Effect of the Observation Height on the Absorbance of Aluminum.

Slit Setting	0.7 nm
Light Source	Hollow Cathode Lamp
D.C. Current	Multi-element 30 m.a. Single-element 25 m.a.
Flame Type	N ₂ - Acetylene
N ₂ O Flowmeter Setting	5.0 (10.4 L/min)
Acetylene Flowmeter Setting (Steel ball)	3.5 (4.4 L/min) Reducing Flame (rich, red)
Observation Height	10.0 mm
Linear Working Range	0 to 60 ppm
Detection Limit	0.061 ppm

c. Notes

The usual used oil sample will contain less than 15 ppm Cr. Therefore, it is recommended that the working curve be determined with zero and 10 ppm standards with the 10 ppm standard reading 50% of full scale. Samples containing zero to 20 ppm Cr can then be analyzed routinely. The threshold criteria for most turbine engines is between 5 and 15 ppm Cr.

d. Other Analytical Lines

<u>Wavelength</u>	<u>Slit</u>	<u>Relative Sensitivity</u>
357.9 nm (UV)	0.7 nm	1.0
359.4 nm (UV)	0.7 nm	1.7
360.5 nm (UV)	0.7 nm	2.2
425.4 nm (VIS)	0.7 nm	3.0
427.5 nm (VIS)	0.7 nm	3.8
429.0 nm (VIS)	0.7 nm	4.5

Figures 45 and 46 show the working curve and the effect of observation height for AA determinations of chromium.

4. STANDARD CONDITIONS FOR COPPER

a. Standard Solutions

Oil calibration standards supplied by the JOAP TSC NAS, Pensacola, FL, contain copper. The standard solutions are prepared by dissolving each desired standard in MIBK using 4 parts

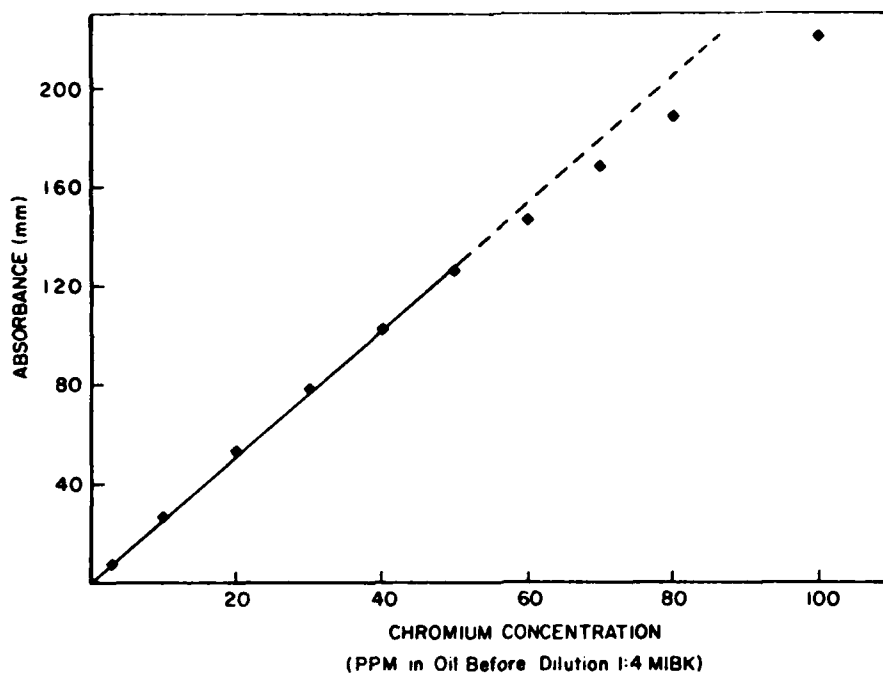


Figure 45. Working Curve for Chromium.

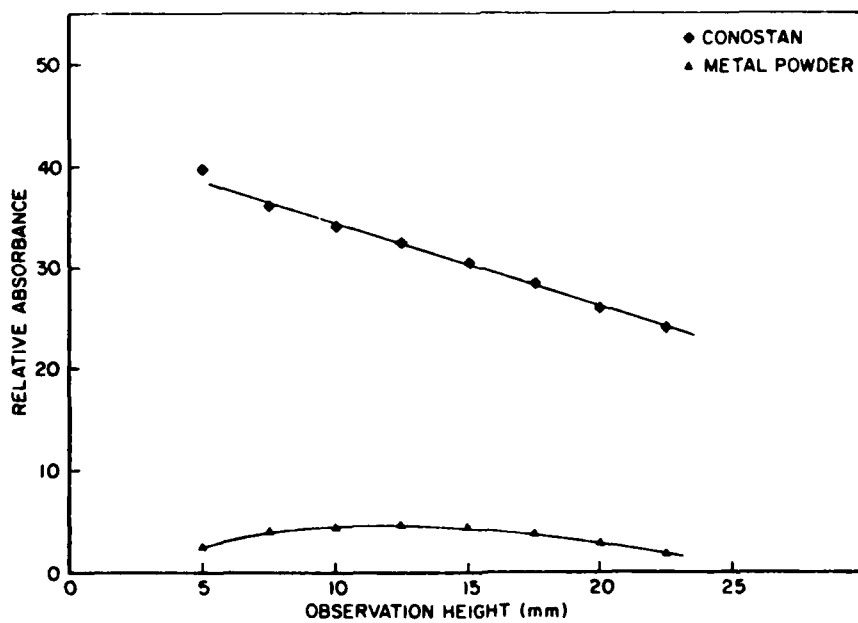


Figure 46. Effect of the Observation Height on the Absorbance of Chromium.

(by weight) MIBK for each part (by weight) standard. Standard solutions should be freshly prepared each day the analyses are to be run.

b. Operating Parameters

Instrument	Atomic Absorption
Wavelength	324.7 nm
Grating	UV
Slit Setting	0.7 nm (0.2 nm)
Light Source	Hollow Cathode Lamp
D.C. Current	Multi-element 30 m.a. Single-element 15 m.a.
Flame Type	Nitrous Oxide - Acetylene
N ₂ O Flowmeter Setting	5.0 (10.4 L/min)
Acetylene Flowmeter Setting (Steel ball)	2.0 (1.4 L/min) oxidizing flame
Observation Height	5 mm
Linear Working Range	0 to 80 ppm
Detection Limit	0.075 ppm

c. Notes

With multi-element lamps containing nickel or iron, a 0.2 nm spectral slit width should be used. The usual used oil sample will contain less than 20 ppm Cu. Therefore, it is recommended that the working curve be determined with zero and 30 ppm standards with the instrument set so that the 30 ppm standard reads full scale. Samples containing 0 to 30 ppm Cu can then be analyzed routinely. The threshold criteria for most turbine engines is between 4 and 15 ppm.

d. Other Analytical Lines

<u>Wavelength</u>	<u>Slit</u>	<u>Relative Sensitivity</u>
324.8 nm	0.7 nm	1.0
327.4 nm	0.7 nm	2.0
216.5 nm	0.2 nm	6.0
222.6 nm	0.2 nm	15.
249.2 nm	0.7 nm	72.
224.4 nm	0.2 nm	157.
244.2 nm	0.7 nm	291.

Figures 47 and 48 show the working curve and the effect of observation height for AA determinations of copper.

5. STANDARD CONDITIONS FOR IRON

a. Standard Solutions

Oil calibration standards supplied by the JOAP TSC, NAS, Pensacola, FL, contain iron. The standard solutions are prepared by dissolving each desired standard in MIBK using 4 parts (by weight) MIBK for each part (by weight) standard. Standard solutions should be freshly prepared each day the analyses are to be run.

b. Operating Parameters

Instrument	Atomic Absorption
Wavelength	248.3 nm
Grating	UV
Slit Setting	0.2 nm
Light Source	Hollow Cathode Lamp
D.C. Current	Multi-element 30 m.a. Single-element
Flame	Nitrous Oxide - Acetylene
N ₂ O Flowmeter Setting	5.0 (10.4 L/min)
Acetylene Flowmeter Setting (Steel ball)	3.5 (4.4 L/min)
Observation Height	5 mm
Linear Working Range	0 to 50 ppm (at 1:4 dilution)
Detection Limit	0.1 ppm

c. Notes

The usual used oil sample will contain less than 50 ppm Fe. Therefore, it is recommended that the working curve be determined with a zero and a 50 ppm standard with the 50 ppm standard reading full scale. The threshold criteria for most turbine engines is between 12 and 40 ppm. Once in a while samples will be encountered which contain over 50 ppm Fe. The samples will need to be diluted or the curve correction controls used in order to accurately determine Fe concentrations between 50 and 100 ppm.

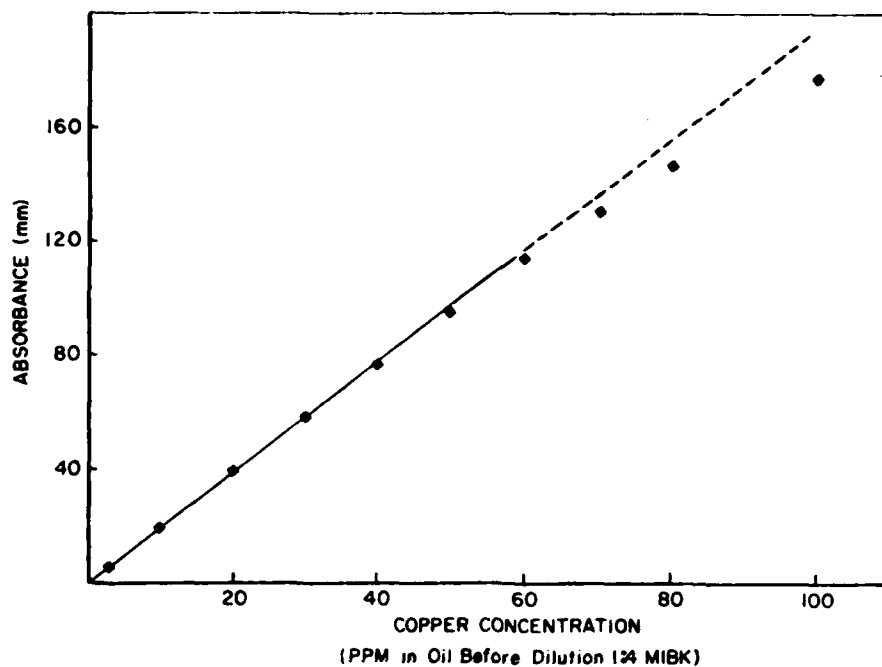


Figure 47. Working Curve for Copper.

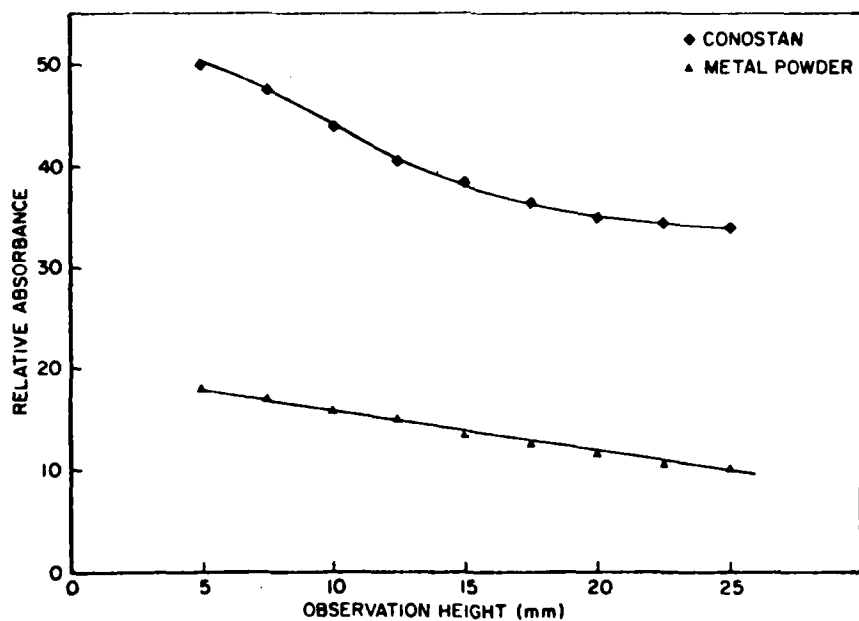


Figure 48. Effect of the Observation Height on the Absorbance of Copper.

d. Other Analytical Lines

<u>Wavelength</u>	<u>Slit</u>	<u>Relative Sensitivity</u>
248.3 nm	0.2 nm	1.0
248.8 nm	0.2 nm	1.7
302.1 nm } 302.1 nm }	0.2 nm	3.7
252.7 nm	0.2 nm	4.6
372.0 nm	0.2 nm	5.7
373.7 nm	0.2 nm	10.
344.1 nm } 344.1 nm }	0.2 nm	14.
305.9 nm	0.2 nm	23.
346.6 nm	0.2 nm	110.
392.0 nm	0.2 nm	130.

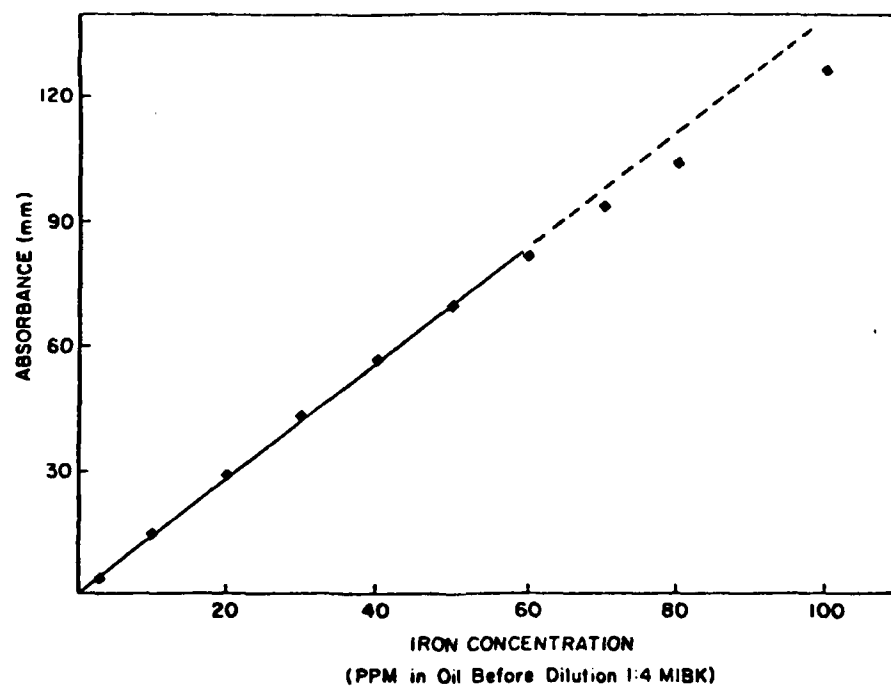


Figure 49. Working Curve for Iron

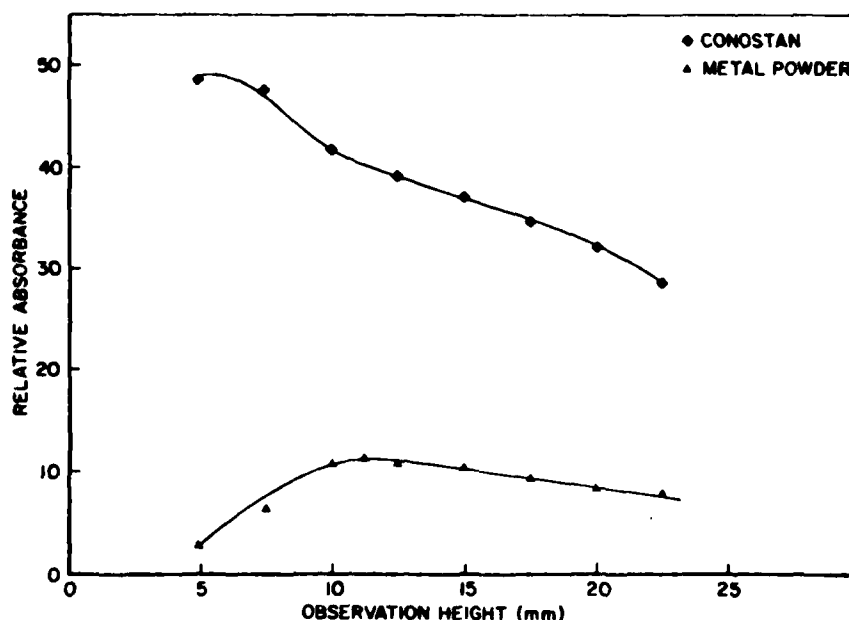


Figure 50. Effect of the Observation Height on the Absorbance of Iron.

6. STANDARD CONDITIONS FOR MAGNESIUM

a. Standard Solutions

Oil calibration standards supplied by the JOAP TSC, NAS, Pensacola, FL, contain magnesium. The standard solutions are prepared by dissolving each desired standard in MIBK using 4 parts (by weight) MIBK for each part (by weight) standard. Standard solutions should be freshly prepared each day the analyses are to be run.

b. Burner Head

The burner head should be rotated 90° for the analysis of Mg. Loosen the burner head and rotate 90°. Re-position the burner head so that it is secured by the positioning pin and the burner slot is now perpendicular to the light beam. If the burner head is seated well you cannot rotate it by hand. Lock the burner head in position.

c. Operating Parameters

Instrument	Atomic Absorption
Wavelength	285.2 nm
Grating	UV
Slit Setting	0.7 nm
Light Source	Hollow Cathode Lamp
D.C. Current	Multi-element 30 m.a. Single-element 6 m.a.
Flame	Nitrous Oxide-Acetylene
N ₂ O Flowmeter Setting	5.0 (10.4 L/min)
Acetylene Flowmeter Setting (Steel ball)	3.0 (3.7 L/min)
Observation Height	10-15 mm
Linear Working Range	0 to 80 ppm
Detection Limit	0.07 ppm

d. Notes

In the usual used oil sample the concentration of Mg is less than 50 ppm. Therefore, it is recommended that the working curve be determined with a zero and 50 ppm standard. The threshold criteria for Mg can be as low as 4 ppm and as high as 50 ppm. Occasionally samples will be encountered with Mg concentrations higher than 50 ppm. In such cases the instrument will have to be adjusted so that higher concentrations can be analyzed or the sample should be diluted and reanalyzed.

e. Other Analytical Lines

<u>Wavelength</u>	<u>Slit</u>	<u>Relative Sensitivity</u>
285.2 nm	0.7 nm	1.0
202.6 nm	0.7 nm	24.

Figures 51 and 52 show the working curve and the effect of observation height for AA determinations of magnesium.

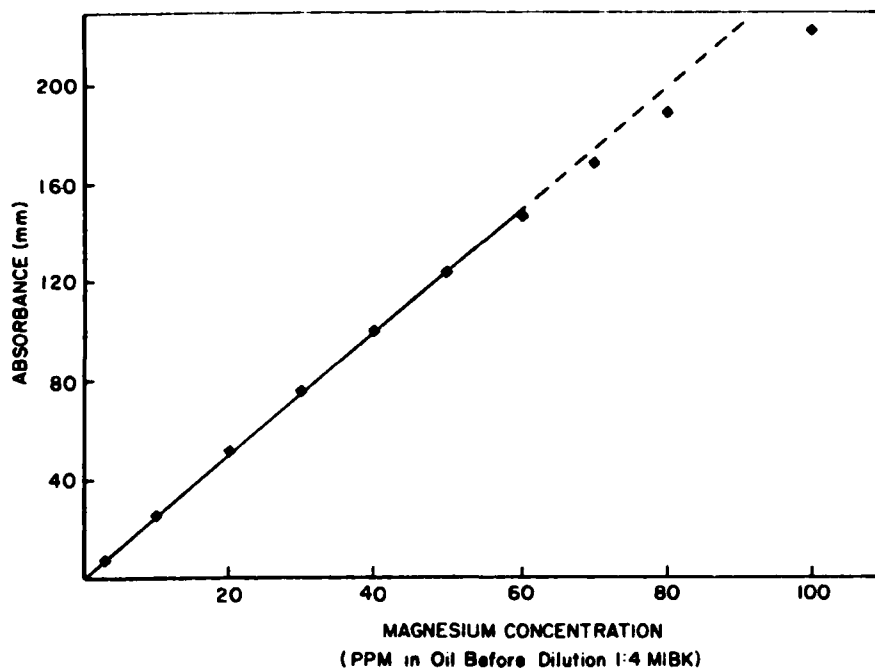


Figure 51. Working Curve for Magnesium.

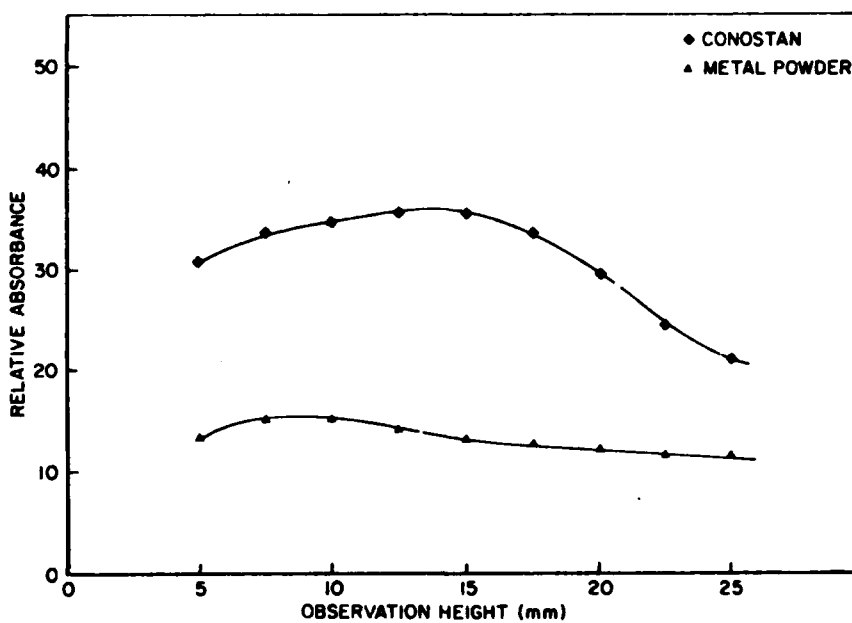


Figure 52. Effect of the Observation Height on the Absorbance of Magnesium.

7. STANDARD CONDITIONS FOR MOLYBDENUM

a. Standard Solutions

Oil calibration standards supplied by the JOAP, TSC, NAS, Pensacola, FL, contain molybdenum. Standard solutions are prepared by dissolving each desired standard in MIBK using 4 parts MIBK for each part standard. These standard solutions are adequate for the analysis of correlation samples.

b. Acid Digestion

Accurate AA analysis of Mo wear metal is impossible as long as the wear metal is present as particulates. Therefore, the acid dissolution procedure is mandated for the AA analysis of Mo.

c. Standards for the Acid Dissolution Method

Each oil calibration standard desired is prepared by adding 0.2 g acid ($\text{HF}/\text{HNO}_3/\text{HCl}$) and 5.8 g solvent (Neodol 91-6/MIBK) to each gram of standard.

d. Samples

For accurate analysis at least 2 g of the used oil sample should be weighed into a linear polyethylene bottle equipped with a polypropylene screw cap. Acid is added (0.2 g per gram of oil) and then the sample is shaken. The sample is then placed in an ultrasonic bath which has been heated to 65°C and ultrasonically agitated for 45 min. After agitation the sample is diluted with solvent (Neodol 91-6/MIBK) (5.8 g per gram of sample) and analyzed by AA in the usual manner.

e. Operating Parameters

Instrument	Atomic Absorption
Wavelength	313.6 nm
Grating	UV
Slit Setting	0.7 nm
Light Source	Hollow Cathode Lamp
D.C. Current	Single-element 30 m.a.

Flame	Nitrous Oxide - Acetylene
N ₂ O Flowmeter Setting	5.0 (10.4 L/min)
Acetylene Flowmeter Setting	4.0 (5.2 L/min)
	Reducing flame
Observation Height	10 mm
Linear Working Range	0 to 100 ppm
Detection Limit	0.05 ppm

f. Notes

Only certain aircraft engines contain Mo. Therefore, the Mo concentration is usually not determined on a routine basis. In turbine engines which contain Mo parts the concentration of Mo is usually less than 20 ppm.

g. Other Analytical Lines

<u>Wavelength</u>	<u>Slit</u>	<u>Relative Sensitivity</u>
313.3 nm	0.7 nm	1.0
317.0 nm	0.7 nm	1.6
379.8 nm	0.7 nm	1.8
319.4 nm	0.7 nm	2.0
386.4 nm	0.7 nm	2.5
390.3 nm	0.7 nm	3.3
315.8 nm	0.7 nm	4.0
320.9 nm	0.2 nm	8.7
311.2 nm	0.2 nm	20.

Figures 53 and 54 show the working curve and the effect of observation height for AA determinations of molybdenum.

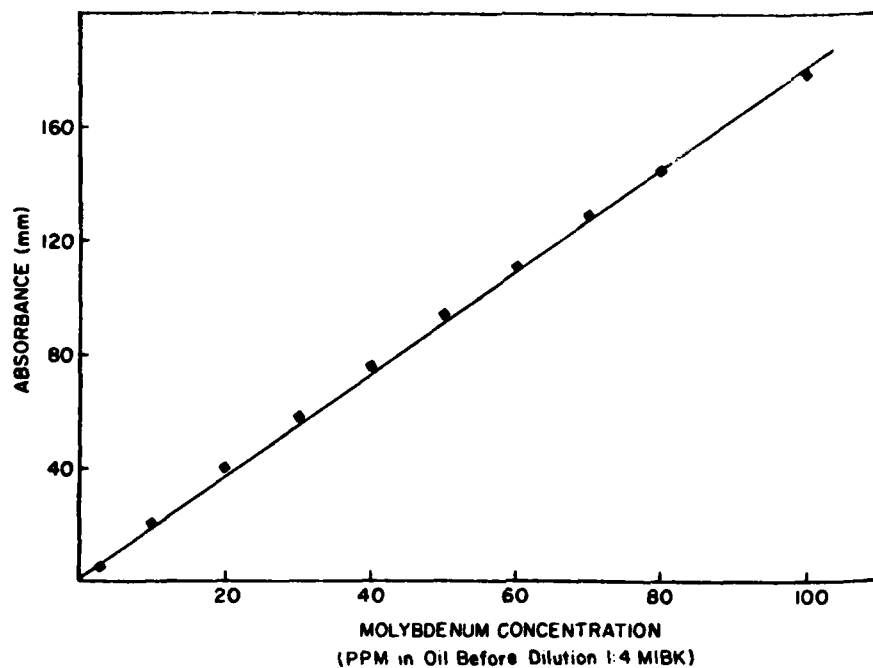


Figure 53. Working Curve for Molybdenum.

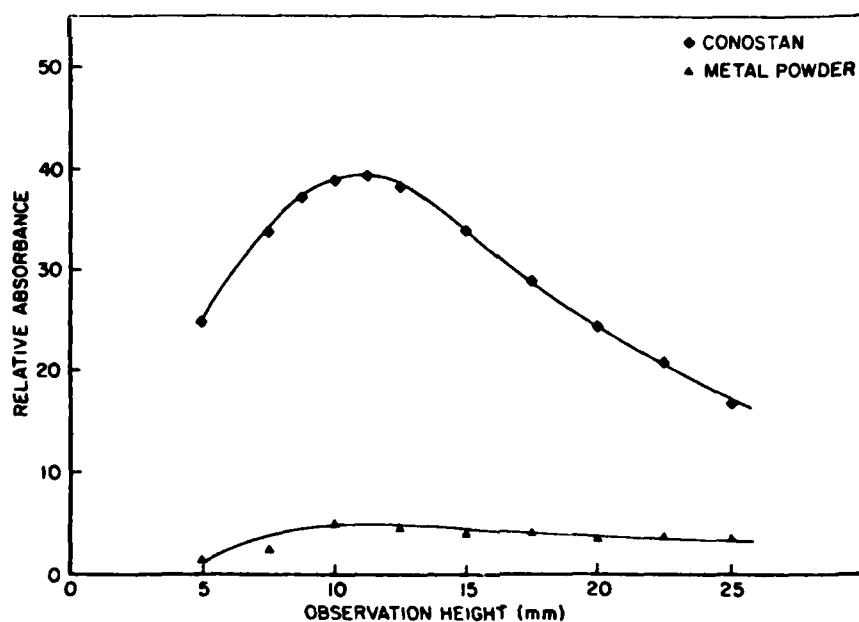


Figure 54. Effect of the Observation Height on the Absorbance of Molybdenum.

8. STANDARD CONDITIONS FOR NICKEL

a. Standard Solutions

Oil calibration standards supplied by the JOAP TSC, NAS, Pensacola, FL, contain nickel. The standard solutions are prepared by dissolving each desired standard in MIBK using 4 parts (by weight) MIBK for each part (by weight) standard. Standard solutions should be freshly prepared each day the analyses are to be run.

b. Operating Parameters

Instrument	Atomic Absorption
Wavelength	341.5 nm
Grating	UV
Slit Setting	0.2 nm
Light Source	Hollow Cathode Lamp
D.C. Current	Single-element 25 m.a.
Flame	Nitrous Oxide Acetylene
N ₂ O Flowmeter Setting	5.0 (10.4 L/min)
Acetylene Flowmeter Setting (Steel ball)	3.8 (4.8 L/min) Reducing
Observation Height	8 mm
Linear Working Range	0 to 100
Detection Limit	0.31 ppm

c. Notes

The most sensitive nickel line is at 232 nm but precision and accuracy are not as good because of the background absorption by the flame.

The usual used oil sample contains very low concentrations of Ni (less than 2 ppm) therefore, it is recommended that the working curve be determined with a zero, a 3 and a 10 ppm standard.

With multi-element lamps containing iron, an interference may occur when the 232 line is used. This fact is another reason the 341.5 nm line is recommended.

d. Other Analytical Lines

<u>Wavelength</u>	<u>Slit</u>	<u>Relative Sensitivity</u>
232.0 nm	0.2 nm	1.0
231.1 nm	0.2 nm	1.5
352.5 nm	0.2 nm	3.3
341.5 nm	0.2 nm	3.5
305.1 nm	0.2 nm	4.5
346.2 nm	0.2 nm	6.6
351.5 nm	0.2 nm	8.1
303.8 nm	0.2 nm	12.
337.0 nm	0.2 nm	17.
323.3 nm	0.2 nm	29.
294.4 nm	0.7 nm	54.

Figures 55 and 56 show the working curve and the effect of observation height for AA determinations of nickel.

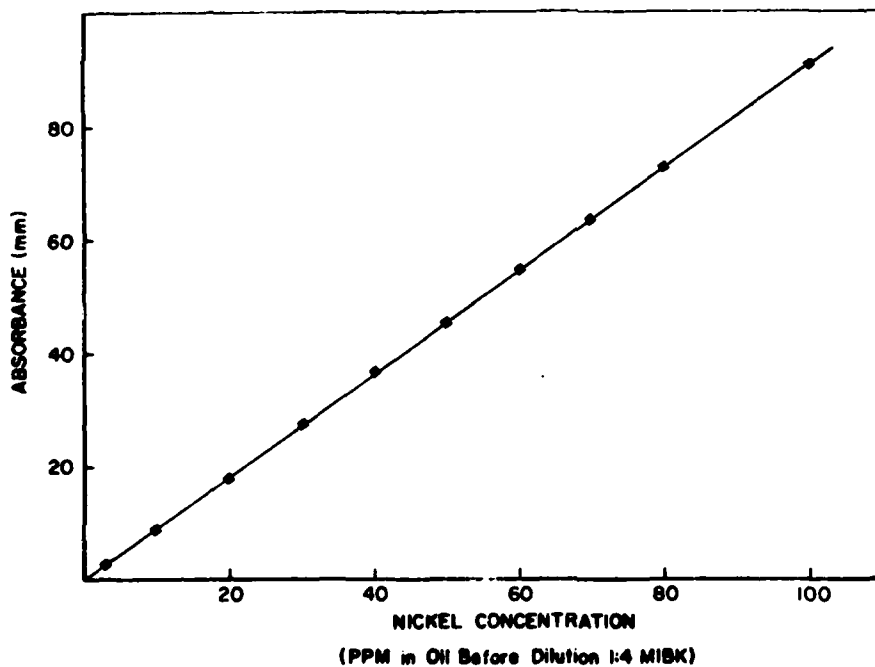


Figure 55. Working Curve for Nickel.

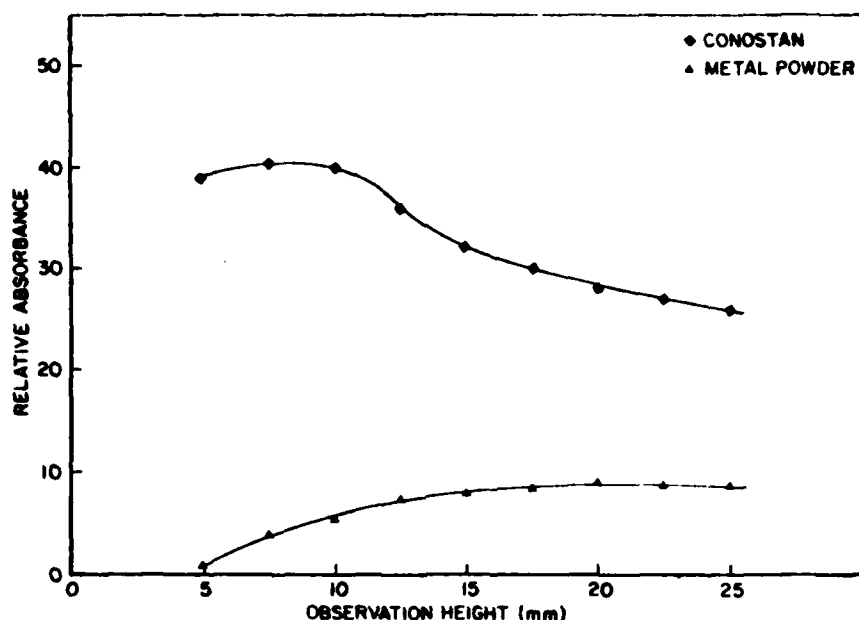


Figure 56. Effect of the Observation Height on the Absorbance of Nickel.

9. STANDARD CONDITIONS FOR LEAD

a. Standard Solutions

Oil calibration standards supplied by the JOAP TSC, NAS, Pensacola, FL, contain lead. The standard solutions are prepared by dissolving each desired standard in MIBK using 4 parts (by weight) MIBK for each part (by weight) standard. Standard solutions should be freshly prepared each day the analyses are to be run.

b. Operating Parameters

Instrument	Atomic Absorption
Wavelength	283.3 nm
Grating	UV
Slit Setting	0.7 nm
Light Source	Hollow Cathode Lamp
D.C. Current	Single-element 12 m.a.
Flame	Nitrous Oxide - Acetylene
N ₂ O Flowmeter Setting	5.0 (10.4 L/min)
Acetylene Flowmeter Setting	3.5 (4.4 L/min)

Observation Height	8 mm
Linear Working Range	0 to 100
Detection Limit	0.92 ppm

c. Notes

Lead concentrations in synthetic turbine engine oils are usually below 20 ppm. However, the lead concentration in lubricating oils from reciprocating engines can be extremely high, well over 1000 ppm.

d. Other Analytical Lines

<u>Wavelength</u>	<u>Slit</u>	<u>Relative Sensitivity</u>
283.3 nm	0.7 nm	1.0
217.0 nm	0.7 nm	0.4
261.4 nm	0.7 nm	10.
368.4 nm	0.7 nm	25.

Figures 57 and 58 show the working curve and the effect of observation height for AA determinations of lead.

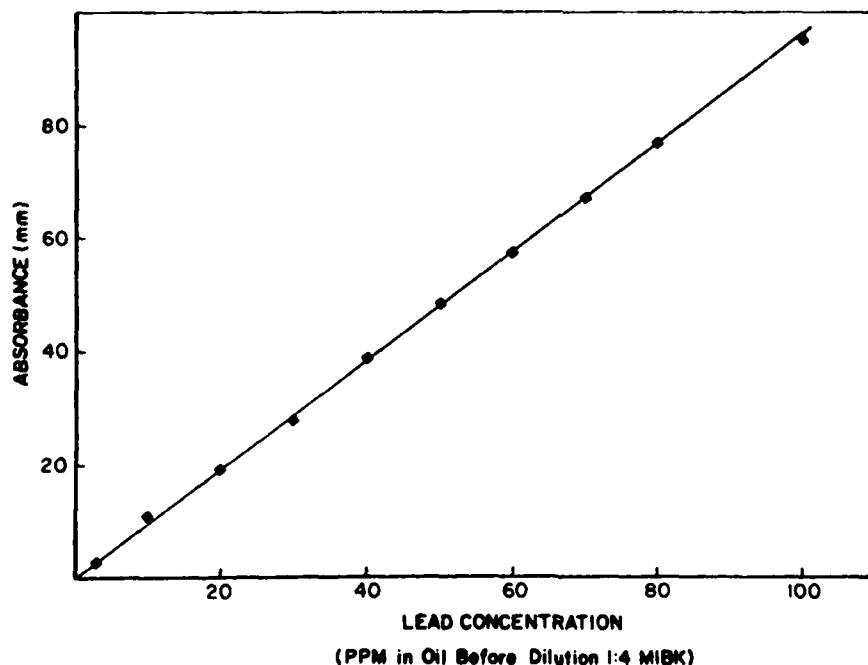


Figure 57. Working Curve for Lead.

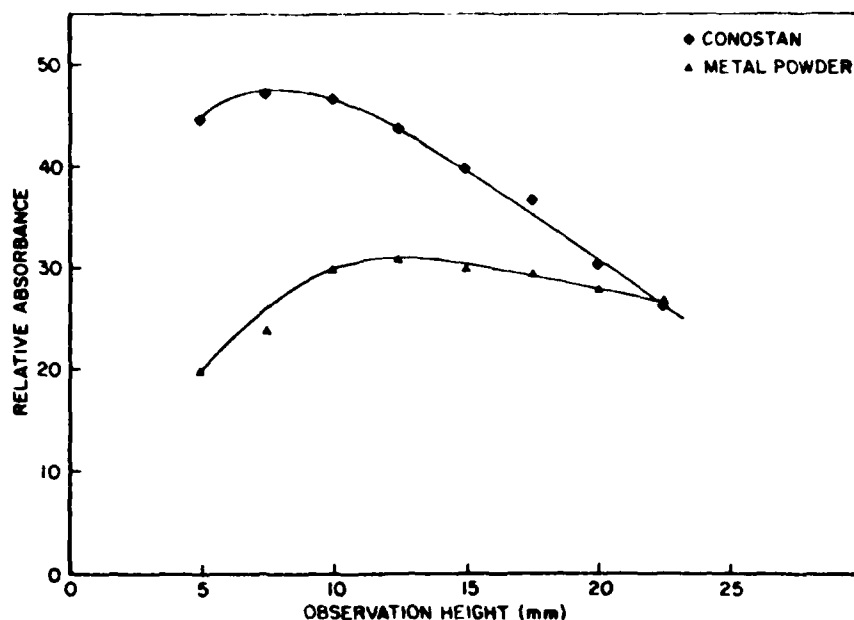


Figure 58. Effect of the Observation Height on the Absorbance of Lead.

10. STANDARD CONDITIONS FOR SILICON

a. Standard Solutions

Oil calibration standards supplied by the JOAP TSC, NAS, Pensacola, FL, contain silicon. The standard solutions are prepared by dissolving each desired standard in MIBK using 4 parts (by weight) MIBK for each part (by weight) standard. Standard solutions should be freshly prepared each day the analyses are to be run.

b. Operating Parameters

Instrument	Atomic Absorption
Wavelength	251.6 nm
Grating	UV
Slit Setting	0.2 nm
Light Source	Hollow Cathode Lamp
D.C. Current	Single-element 40 m.a.
Flame	Nitrous Oxide - Acetylene
N ₂ O Flowmeter Setting	5.0 (10.4 L/min)
Acetylene Flowmeter Setting (Steel ball)	4.0 (5.2 L/min)

Observation Height	10 mm
Linear Working Range	0 to 100 ppm
Detection Limit	0.65 ppm

c. Notes

The concentration of Si in the typical used oil sample will be below 10 ppm. High Si concentrations are usually indicative of external (dust, sand, etc) contamination and indicate that an oil change is in order.

d. Other Analytical Lines

<u>Wavelength</u>	<u>Slit</u>	<u>Relative Sensitivity</u>
251.6 nm	0.2 nm	1.0
250.7 nm	0.7 nm	2.8
252.8 nm	0.2 nm	3.2
252.4 nm	0.2 nm	3.7
221.1 nm	0.2 nm	4.3
221.1 nm	0.2 nm	8.

Figures 59 and 60 show the working curve and the effect of observation height for AA determinations of silicon.

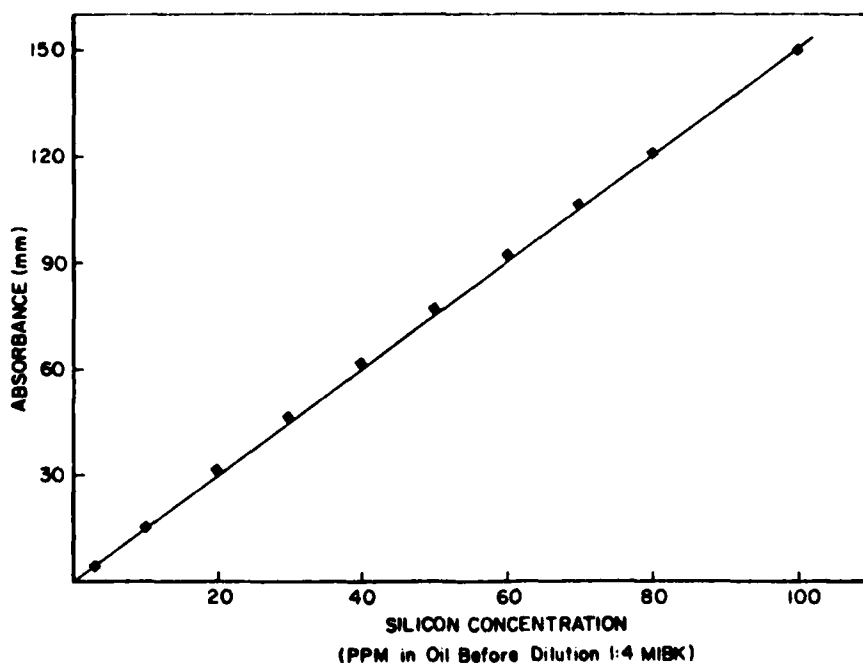


Figure 59. Working Curve for Silicon.

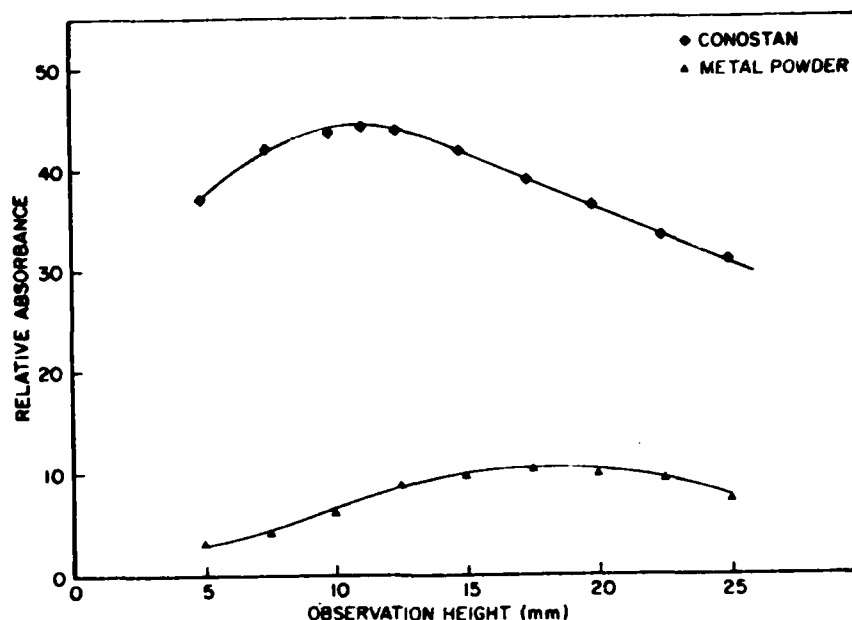


Figure 60. Effect of the Observation Height on the Absorbance of Silicon.

11. STANDARD CONDITIONS FOR TIN

a. Standard Solutions

Oil calibration standards supplied by the JOAP TSC, NAS, Pensacola, FL, contain tin. The standard solutions are prepared by dissolving each desired standard in MIBK using 4 parts (by weight) MIBK for each part (by weight) standard. Standard solutions should be freshly prepared each day the analyses are to be run.

b. Operating Parameters

Instrument	Atomic Absorption
Wavelength	286.3
Grating	UV
Slit Setting	0.7 nm
Light Source	Hollow Cathode Lamp
D.C. Current	Single-element 30 m.a.
Flame	Nitrous Oxide - Acetylene
N ₂ O Flowmeter Setting	5.0 (10.4 L/min)

Acetylene Flowmeter Setting (Steel ball)	4.0 (5.2 L/min)
Observation Height	8 mm
Linear Working Range	0 to 100
Detection Limit	1.60 ppm

c. Notes

The most sensitive Sn line is at 224.6 nm, but precision and accuracy are not as good because of background absorption by the flame. Tin concentrations in used turbine engine lubricants are very low (less than 5 ppm) and are usually not determined on a routine basis.

d. Other Analytical Lines

<u>Wavelength</u>	<u>Slit</u>	<u>Relative Sensitivity</u>
224.6 nm	0.2 nm	1.0
286.3 nm	0.7 nm	1.8
235.5 nm	0.7 nm	1.6
270.6 nm	0.7 nm	2.9
303.4 nm	0.2 nm	3.8
254.7 nm	0.7 nm	5.4
219.9 nm	0.2 nm	5.7
300.9 nm	0.7 nm	6.9
233.5 nm	0.7 nm	6.9
266.1 nm	0.7 nm	29.

Figures 61 and 62 show the working curve and the effect of observation height for AA determinations of tin.

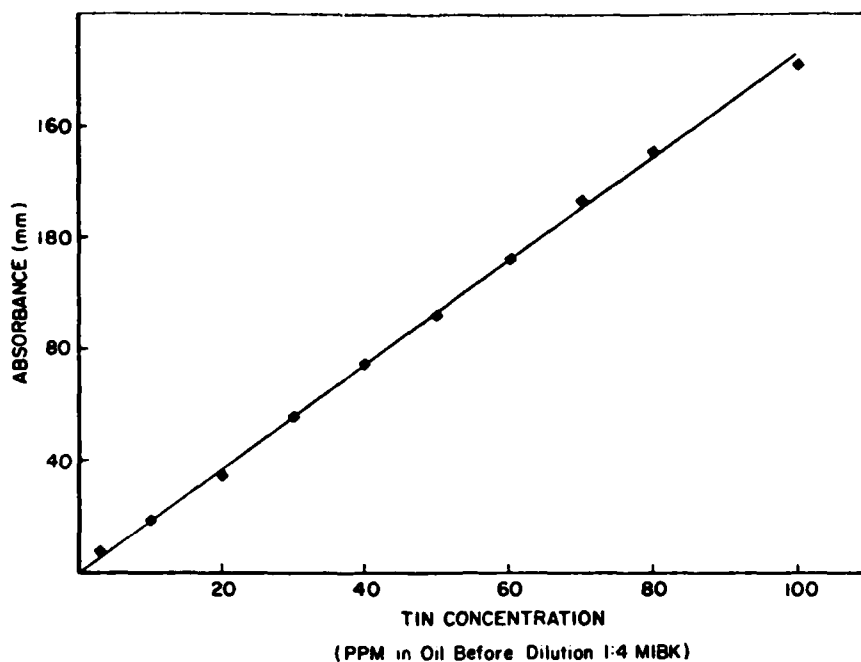


Figure 61. Working Curve for Tin.

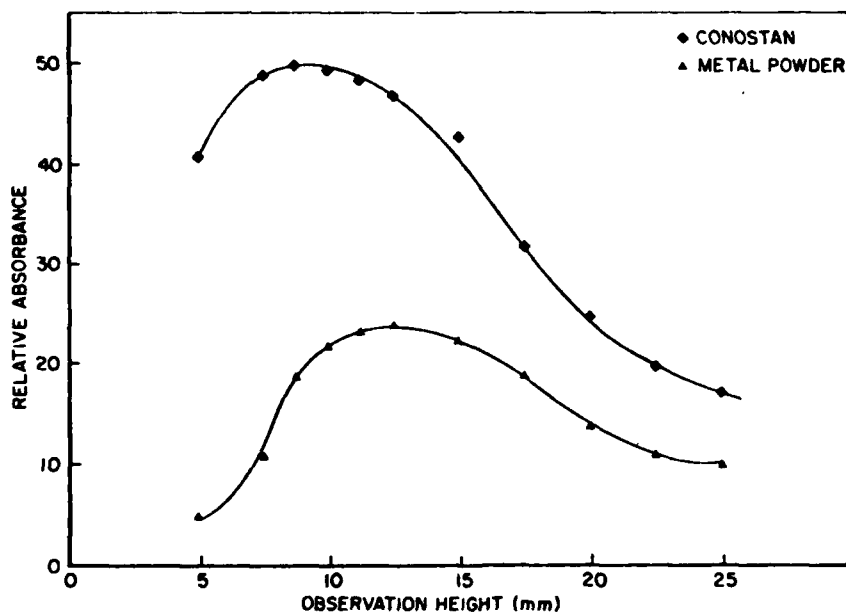


Figure 62. Effect of the Observation Height on the Absorbance of Tin.

12. STANDARD CONDITIONS FOR TITANIUM

a. Standard Solutions

All oil calibration standards supplied by the JOAP TSC, NAS, Pensacola, FL, contain titanium. Standard solutions for direct analysis are prepared by dissolving each desired standard in MIBK using 4 parts MIBK for each part standard.

b. Acid Dissolution Method

Accurate AA Analysis of Ti wear metal is impossible as long as it is present as metallic particulates. Therefore, the acid dissolution procedure is required to obtain an accurate analysis of Ti.

c. Standards for the Acid Dissolution Method

Each oil calibration standard desired is prepared by adding 0.2 g acid ($\text{HF}/\text{HNO}_3/\text{HCl}$) and 5.8 g solvent (Neodol 91-6/MIBK) to each gram of standard.

d. Samples

For accurate analyses, at least 2 g of used oil sample should be weighed into a linear polyethylene bottle equipped with a polypropylene screw cap. Acid is added (0.2 g per gram sample) and then the sample is hand shaken. The sample is placed in a vortex mixer and agitated for 5 minutes at room temperature. After agitation the sample is diluted with solvent (5.8 g per gram of oil) and analyzed by AA.

e. Operating Parameters

Instrument	Atomic Absorption
Wavelength	365.4
Grating	UV
Slit Setting	0.2 nm
Light Source	Hollow Cathode Lamp
D.C. Current	Single-element 40 m.a.
Flame	Nitrous Oxide Acetylene
N ₂ O Flowmeter Setting	5.0 (10.4 L/min)
Acetylene Flowmeter Setting (Steel ball)	4.0 (5.2 L/min)

Observation Height	12 mm
Linear Working Range	0 to 100 ppm
Detection Limit	0.49 ppm

f. Notes

Only certain aircraft engines contain Ti. Therefore, Ti concentrations are determined only for specific engines. In aircraft engines containing Ti components concentration of Ti should never be higher than 20 ppm since threshold values range between 2 and 16 ppm. Accurate determinations of Ti are important since trends are more indicative of wear than the actual concentrations.

g. Other Analytical Lines

<u>Wavelength</u>	<u>Slit</u>	<u>Relative Sensitivity</u>
365.4 nm	0.2 nm	1.0
364.3 nm	0.2 nm	1.1
320.0 nm	0.2 nm	1.2
363.6 nm	0.2 nm	1.2
335.5 nm	0.2 nm	1.4
375.3 nm	0.2 nm	1.6
334.2 nm	0.2 nm	1.6
399.9 nm	0.2 nm	1.6
399.0 nm	0.2 nm	1.9

Figures 63 and 64 show the working curve and the effect of observation height for AA determinations of titanium.

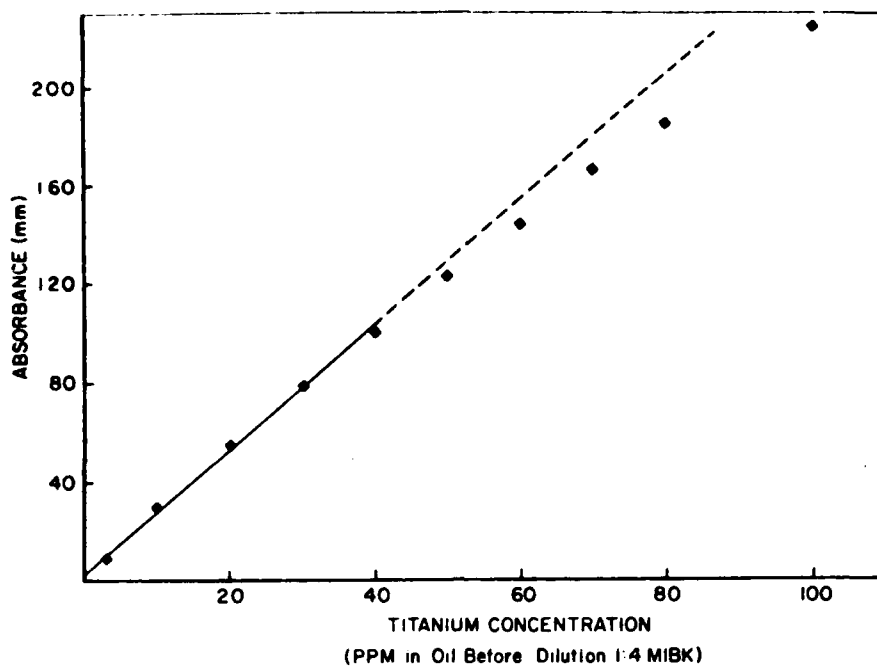


Figure 63. Working Curve for Titanium

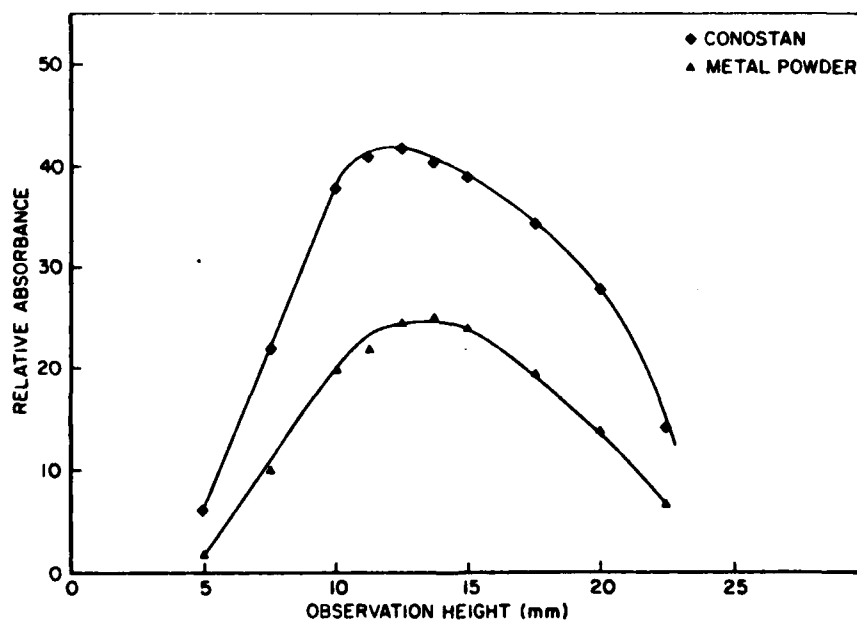


Figure 64. Effect of the Observation Height on the Absorbance of Titanium

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